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OF THE

ROYAL SOCIETY

OF

NEW SOUTH WALES

FOR

1931.

(INCORPORATED 1881.)

VOL. LXV.

EDITED BY

THE HONORARY SECRETARIES.

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN.

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1932.

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VOLUME LXV.

NOTICE.

THE ROYAL SOCIETY of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australian Philosophical Society," by which title it was known until 1856, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

TO AUTHORS.

Authors should submit their papers in typescript and in a condition ready for printing. All physico-chemical symbols and mathematical formulæ should be so clearly written that the compositor should find no difficulty in reading the manuscript. Sectional headings and tabular matter should not be underlined. Pen-illustrations accompanying papers should be made with black Indian ink upon smooth white Bristol board. Lettering and numbers should be such that, when the illustration or graph is reduced to $3\frac{1}{2}$ inches in width, the lettering will be quite legible. On graphs and text figures any lettering may be lightly inserted in pencil. Photomicrographs should be rectangular rather than circular, to obviate too great a reduction. The size of a full page plate in the Journal is $4 \times 6\frac{1}{4}$ inches, and the general reduction of illustrations to this limit should be considered by authors. When drawings, etc., are submitted in a state unsuitable for reproduction, the cost of the preparation of such drawings for the process-block maker must be borne by the author. The cost of colouring plates or maps must also be borne by the author.

FORM OF BEQUEST.

I bequeath the sum of £   to the ROYAL SOCIETY OF NEW SOUTH WALES, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within   calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[*Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.*]

PUBLICATIONS.

The following publications of the Society, if in print, can be obtained at the Society's Rooms, Science House, Gloucester and Essex Streets, Sydney.

Transactions of the Philosophical Society, N.S.W., 1862-5, pp. 374, out of print.

Vols. I—XI	Transactions of the Royal Society, N.S.W.,				1867—1877		,,
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LIST OF THE MEMBERS

OF THE

Royal Society of New South Wales.

P Members who have contributed papers which have been published in the Society Journal. The numerals indicate the number of such contributions.

‡ Life Members.

Elected.		
1908		Abbott, George Henry, B.A., M.B., Ch.M., 185 Macquarie-street p.r. 'Cooringa,' 252 Liverpool Road, Summer Hill.
1904		Adams, William John, M.I.Mech.E., 175 Clarence-street.
1898		Alexander, Frank Lee, William-street, Granville.
1905	P 3	Anderson, Charles, M.A., D.Sc. *Edin.*, Director of the Australian Museum, College-street. (President, 1924.)
1909	P 9	Andrews, Ernest C., B.A., F.G.S., Hon. Mem. Washington Academy of Sciences, Government Geologist, Department of Mines, Sydney: p.r. 32 Benelong Crescent, Bellevue Hill. (President, 1921.)
1930		Aston, Ronald Leslie, B.Sc., B.E. *Syd.*, M.Sc. *Cantab.*, Lecturer in Civil Engineering and Surveying in the University of Sydney, 24 Redmyre Road, Strathfield.
1919		Aurousseau, Marcel, B.Sc., No. 65A Market-lane, Manly.
1923		Baccarini. Antonio, Doctor in Chemistry *Florence*, c/o Dante, Alighieri Society, Box 1168, G.P.O. Sydney.
1878		Backhouse, His Honour Judge A. P., M.A., 'Melita,' Elizabeth Bay.
1924		Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Assoc.-Professor of Physics in the University of Sydney.
1919		Baker, Henry Herbert, Watson House, Bligh-street, Sydney.
1894	P 28	Baker, Richard Thomas, The Crescent, Cheltenham.
1926		Bannon, Joseph, B.Sc. Demonstrator in Physics in the University of Sydney; p.r. 'Dunisla,' The Crescent, Homebush.
1919		Bardsley, John Ralph, 'The Pines,' Lea Avenue, Five Dock.
1925		Barker-Woden, Lucien, F.R.G.S., Commonwealth Department of Navigation, William Street, Melbourne.
1908	P 1	Barling, John, L.S., 'St. Adrians,' Raglan-street, Mosman.
1895	P 9	Barraclough, Sir Henry, K.B.E., B.E., M.M.E., M. Inst. C.E., M. I. Mech. E., Memb. Soc. Promotion Eng. Education; Memb. Internat. Assoc. Testing Materials; Dean of the Faculty of Engineering and Professor of Mechanical Engineering in the University of Sydney.
1929		Baur, Fidel George, M.D., Ophthalmic Surgeon, 213 Macquarie-street, Sydney.
1909	P 2	Benson, William Noel, D.Sc. *Syd.*, B.A. *Cantab.*, F.G.S., Professor of Geology in the University of Otago, Dunedin, N.Z.
1926		Bentivoglio, Sydney Ernest, B.Sc.Agr., c/o Tooth and Co., Limited, Sydney; p.r., 14 Gordon Avenue, Coogee.

Elected.		
1919		Bettley-Cooke, Hubert Vernon, F.C.S., A.A.C.I., 'The Hollies,' Minter-street, Canterbury.
1923		Birks, George Frederick, c/o Potter & Birks, 15 Grosvenor-street
1916		Birrell, Septimus, Appian Way, Burwood.
1920		Bishop, Eldred George, 8 Belmont-road, Mosman.
1915		Bishop, John, 12 O'Connell-street.
1923	P 4	Blakely, William Faris, 'Myola,' Florence-street, Hornsby.
1905		Blakemore, George Henry, "Wawoona," 10 Cooper Street, Strathfield.
1888		‡Blaxland, Walter, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, 'Inglewood,' Florida Road, Palm Beach, Sydney.
1926	P 4	Booker, Frederick William, B.Sc., 'Dunkeld,' Nicholson-street, Chatswood.
1920	P 4	Booth, Edgar Harold, M.C., B.Sc., F.Inst.P., Lecturer and Demonstrator in Physics in the University of Sydney.
1922		Bradfield, John Job Crew, D.Sc. Eng., M.E., M. Inst. C.E., M.Inst.E.*Aust.*, Chief Engineer, Metropolitan Railway Construction, Railway Department, Sydney.
1926		Branch, Kenneth James F., 99 Ocean Beach, Manly.
1917		Breakwell, Ernest, B.A., B.Sc., Dept. of Education, Box 33 A, G.P.O., Sydney.
1891		Brennand, Henry J. W., B.A., M.D., Ch.M. *Syd.*, V.D., Surgeon Commander R.A.N. Ret., 223 Macquarie-street; p.r. 73 Milsons Road, Cremorne.
1923		Brereton, Ernest Le Gay, B.Sc., Lecturer and Demonstrator in Chemistry in the University of Sydney.
1919	P 1	Briggs, George Henry, B.Sc., Ph.D., Assistant-Professor of Physics in the University of Sydney.
1923		Brown, Herbert, 'Sikoti,' Alexander-street, Collaroy Beach, Sydney.
1906		Brown, James B., St. Andrew's, No 1 Maitland Avenue, East Kew, E. 4, Victoria.
1913	P 17	Browne, William Rowan, D.Sc., Assistant-Professor of Geology in the University of Sydney.
1898		‡Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M. B.Sc., *Syd.*, 'Wyoming,' 175 Macquarie-street, Sydney.
1926		Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.
1919	P 10	Burrows, George Joseph, B.Sc., Lecturer and Demonstrator in Chemistry in the University of Sydney; p.r. Watson-street, Neutral Bay.
1929		Caley, Gilbert Fatkin, Manager, Glycerine Distillery Co., Ltd., Alexandria; p.r. 'Windyridge,' Park Road, Auburn.
1929	P 1	Callaghan, Allan Robert, D.Phil., B.Sc., (*Oxon.*), B.Sc.Agr., Plant Breeder, Wagga Experiment Farm, Bomen, N.S.W.
1909		Calvert, Thomas Copley, Assoc.M.Inst.C.E., c/o Dept. of Public Works, Newcastle, N.S.W.
1923		Cameron, Lindsay Duncan, Hilly-street, Mortlake.
1891		Carment, David, F.I.A. *Grt. Brit. & Irel.* F.F.A., *Scot.*, 4 Whaling Road, North Sydney.
1920		Carruthers, Sir Joseph Hector, K.C.M.G., M.L.C., M.A., *Syd.*, LL.D., *St. Andrews*, 'Highbury,' Waverley.

Elected		
1903	P 3	Carslaw, Horatio S., M.A., Sc. D., Professor of Mathematics in the University of Sydney.
1913	P 3	Challinor, Richard Westman, F.I.C., F.C.S., Lecturer in Chemistry, Sydney Technical College.
1909	P 2	Chapman, Henry G., M.D., B.S., Director of Cancer Research, University of Sydney. *Hon. Treasurer.*
1913	P 18	Cheel, Edwin, Curator, National Herbarium, Botanic Gardens, Sydney. *President.*
1925	P 1	Clark, William E., High School, Armidale.
1909	P 20	Cleland, John Burton, M.D., Ch.M., Professor of Pathology in the University of Adelaide. (President 1917.)
1896	P 4	Cook, W. E., M.C.E.*Melb.*, M.Inst.C.E., Burroway St., Neutral Bay.
1920		Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack streets, Sydney.
1913	P 4	Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College; p.r. Bannerman Crescent, Rosebery.
1928		Coppleson, Victor Marcus, M.B., Ch.M., F.R.C.S. ,225 Macquarie-street, Sydney.
1882		Cornwell, Samuel, J.P., 'Capanesk,' Tyagarah, North Coast.
1919		Cotton, Frank Stanley, B.Sc., Chief Lecturer and Demonstrator in Physiology in the University of Sydney.
1909	P 7	Cotton, Leo Arthur, M.A., D.Sc., Professor of Geology in the University of Sydney. *Vice-President.* (President 1929.)
1892	P 1	Cowdery, George R., Assoc.M.Inst.C.E., 'Glencoe,' Torrington Road, Strathfield.
1886		Crago, W. H., M.R.C.S. *Eng.*, L.R.C.P. *Lond.*, 135 Macquarie-st.
1921	P 1	‡Cresswick, John Arthur, 101 Villiers-street, Rockdale.
1925		Curry, Harris Eric Marshall, 8 Lower Wycombe-road, Neutral Bay.
1912		Curtis, Louis Albert, L.S., F.I.S. (N.S.W.), V.D., Room 618, Government Savings Bank Building, Castlereagh-street; p.r. No. 1 Mayfair Flats, Macleay-street, Darlinghurst.
1890		Dare, Henry Harvey, M.E., M.Inst.C.E., Commissioner, Water Conservation and Irrigation Commission, Department of Agriculture Building, Raphael-street, Sydney.
1886	P 23	David, Sir Edgeworth, K.B.E., C.M.G., D.S.O., B.A., D.Sc., F.R.S., F.G.S., Wollaston Medallist, Emeritus Professor of Geology and Physical Geography in the University of Sydney; p.r. 'Coringah,' Burdett-street, Hornsby. (President 1895, 1910.)
1928		Davidson, Walter Charles, General Manager, Clyde Engineering Company, Granville.
1930		Davies, Harold Whitridge M.B., B.S.*Adel.*, Professor of Physiology in the University of Sydney.
1919	P 2	de Beuzeville, Wilfrid Alex. Watt, J.P., 'Mélamere,' Welham-street, Beecroft, N.S.W.
1921		Delprat, Guillaume Daniel, C.B.E., 'Keynsham,' Mandeville Crescent, Toorak, Victoria.
1921		Denison, Sir Hugh Robert, K.B.E., 701 Culwulla Chambers, Castlereagh-street.
1894		Dick, James Adam, C.M.G., B.A. *Syd.*, M.D., Ch.M., F.R.C.S. *Edin.*, 'Catfoss,' 59 Belmore Road, Randwick.

Elected		
1906		‡Dixson, William, 'Merridong,' Gordon Road, Killara.
1913	P 3	Doherty, William M., F.I.C., F.C.S., Second Government Analyst, p.r. 'Jesmond,' George-street, Marrickville.
1928		Donegan, Henry Arthur James, A.S.T.C., Chemical Laboratory, Department of Mines, Sydney.
1908	P 6	Dun, William S., Palæontologist, Department of Mines, Sydney. (President 1918.)
1924		Dupain, George Zephirin, A.A.C.I., F.C.S., Dupain Institute of Physical Education, Manning Building, Pitt and Hay Streets, Sydney, p.r. 'Symington,' Parramatta Road, Ashfield.
1924		Durham, Joseph, 120 Belmore Road, Randwick.
1923	P 9	Earl, John Campbell, D.Sc. Ph.D., Professor of Organic Chemistry in the University of Sydney.
1919		Earp, The Hon. George Frederick, C.B.E., M.L.C., Australia House, 52 Carrington-street.
1924		Eastaugh, Frederick Alldis, A.R.S.M., F.I.C., Assoc. Professor in Chemistry, Assaying and Metallurgy in the University of Sydney.
1916	P 2	Enright, Walter J., B.A., High-street, West Maitland, N.S.W.
1908		Esdaile, Edward William, 42 Hunter-street.
1921		Farnsworth, Henry Gordon, 'Rothsay,' 90 Alt-street, Ashfield.
1910		Farrell, John, A.T.C., *Syd.*, Riverina Flats, 265 Palmer-street, Sydney.
1909	P 7	Fawsitt, Charles Edward, D.Sc., Ph D., Professor of Chemistry in the University of Sydney. (President 1919).
1922		Ferguson, Andrew.
1927	P 3	Finnemore, Horace, B.Sc., F.I.C., Lecturer in Pharmacy in the University of Sydney.
1923		Fiaschi, Piero, O.B.E., M.D. *Columbia Univ.*, D.D.S. *New York*, M.R.C.S. *Eng.*, L.R.C.P. *Lond.*, 178 Phillip-street.
1920		Fisk, Ernest Thomas, Wireless House, 47 York-street.
1888		Fitzhardinge, His Honour Judge G. H., M.A. 'Red Hill,' Pennant Hills.
1879		‡Foreman, Joseph, M.R.C.S. *Eng.* L.R.C.P. *Edin.*, 'The Astor,' Macquarie-street.
1920		Fortescue, Albert John, 'Benambra,' Loftus-street, Arncliffe.
1905		Foy, Mark, c/o Hydro Office, Liverpool and Elizabeth streets, Sydney.
1925		Friend, Norman Bartlett, 48 Pile-street, Dulwich Hill.
1918		Gallagher, James Laurence, M.A. *Syd.*, 'Akaroa,' Ellesmere Avenue, Hunter's Hill.
1926		Gibson, Alexander James, M.E., M.Inst.C.E., M.I E.*Aust.*, 906 Culwulla Chambers, Castlereagh-street, Sydney.
1921		Godfrey, Gordon Hay, M.A., B.Sc. Lecturer in Physics in the Technical College, Sydney; p.r. "Eversham," Victoria Parade, Manly.

Elected		
1897		Gould, The Hon. Sir Albert John, K.B., V.D., 'Eynesbury,' Edgecliff.
1922	P 2	Greig, William Arthur, Mines Department, Sydney.
1923		Gurney, William Butler, B.Sc., F.E.S., Government Entomologist, Department of Agriculture, Sydney.
1880	P 5	Halligan, Gerald H., L.S., F.G.S., "Geraldine," Culworth Avenue, Killara.
1912		Hallmann, E. F., B.Sc., 72 John-street, Petersham.
1892		Halloran, Henry Ferdinand, L.S., 82 Pitt-street.
1919		Hambridge, Frank, Adelaide Steamship Co. Chambers, 22 Bridge-street, Sydney.
1912		Hamilton, Alexander G., 'Tanandra,' Hercules-st., Chatswood.
1909		Hammond, Walter L., B.Sc., High School, Bathurst.
1905	P 5	Harker, George, D.Sc., F.A.C.I., 57 Junction-street, Summer Hill.
1913	P 1	Harper, Leslie F., F.G.S., Geological Surveyor, Department of Mines, Sydney.
1923	P 1	Harrison, Travis Henry, B.Sc.Agr., Lecturer in Entomology and Botany at the Hawkesbury Agricultural College, Richmond; p.r. 17 Hurlstone-avenue, Summer Hill.
1918		Hassan, Alex. Richard Roby.
1929		Hawley, Joseph William, 15 Springdale-road, Killara.
1914		Hector, Alex. Burnet, "Druminard," Greenwich-road, Greenwich.
1916		Henderson, James, 'Dunsfold,' Clanalpine-street, Mosman.
1919		Henriques, Frederick Lester, 208 Clarence-street.
1919	P 2	Henry, Max, D.S.O., B.V.Sc., M.R.C.V.S., Chief Veterinary Surgeon, Dept. Agriculture, Sydney. p.r. 'Coram Cottage,' Essex-street, Epping.
1918		Hindmarsh, Percival, M.A., B.Sc.Agr., Teachers' College, The University, Sydney; p.r. 'Lurnea,' Canberra Avenue, Greenwich.
1921	P 2	Hindmarsh, William Lloyd, B.V.Sc., M.R.C.V.S., D.V.H., District Veterinary Officer, Glenfield.
1928		Hirst, George Walter Cansdell, B.Sc., Chief Mechanical Engineer's Office, N.S.W. Govt. Railways, Wilson Street, Redfern; p.r. 'St Cload,' Beaconsfield-road, Chatswood
1930		Hodson, John S., Electrical Engineer, H.M. Naval Establishments, Garden Island, Sydney.
1916		Hoggan, Henry James, A.M.I.M.E., A.M.I.E. *Aust.*, Manchester Unity Chambers, 160 Castlereagh-street; p.r. 'Lincluden,' Frederick-street, Rockdale.
1924		Holme, Ernest Rudolph, O.B.E., M.A., Professor of English Language in the University of Sydney.
1930		Holmes, James MacDonald, Associate Professor of Geography in the University of Sydney.
1901		Holt, Thomas S., 'Amalfi,' Appian Way, Burwood.
1905	P 3	Hooper, George, J.P., F.T.C. *Syd.*, 'Mycumbene,' Nielsen Park, Vaucluse.
1919		Hoskins, Arthur Sidney, Eskroy Park, Bowenfels.
1919		Hoskins, Cecil Harold, c/o Australian Iron and Steel Co., Ltd., Kembla Building, Margaret-street, Sydney.
1913		Hudson, G. Inglis, J.P., F.C.S. 180 Arden-st., Coogee.

Elected		
1923	P 2	Hynes, Harold John, M.Sc., B.Sc. Agr., Senior Asst. Biologist, Department of Agriculture, Sydney.
1927		Inglis, William Keith, M.D., Ch.M., Lecturer in Pathology in the University of Sydney; p.r. 34 Wolseley-street, Drummoyne.
1922		Jacobs, Ernest Godfried, 'Cambria,' 106 Bland-street, Ashfield.
1904		Jaquet, John Blockley, A.R.S.M., F.G.S., Chief Inspector of Mines, Department of Mines, Sydney.
1929		Jeffrey, Robert Ewen, A.A.C.I., Managing Director, Bardsley's Ltd.; p.r. 9 Greycliffe-avenue, Vaucluse.
1925		Jenkins, Charles Adrian, B.E., B.Sc., 2 Ramsgate Avenue, Bondi Beach.
1917		Jenkins, Richard Ford, Engineer for Boring, Irrigation Commission, 6 Union-street, Mosman.
1918		John, Morgan Jones, M.I.Mech.E., A.M.I.E.E. *Lond.*, M.I.E. *Aust.*, M.I.M. *Aust.*, p.r. Village High Road, Vaucluse.
1909	P 15	Johnston, Thomas Harvey, M.A., D.Sc., F.L.S., C.M.Z.S., Professor of Zoology in the University of Adelaide.
1924		Jones, Leo Joseph, Geological Surveyor, Department of Mines, Sydney.
1930		Judd, William Percy, 49 Hirst Street, Arncliffe.
1911		Julius, George A., Sir, Kt., B.Sc., M.E., M.I.Mech.E., Culwulla Chambers, Castlereagh-street, Sydney.
1924		Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 5 Savings Bank Flats, Bondi Beach.
1887		Kent, Harry C., M.A., F.R.I.B.A., 35 Beresford Road, Rose Bay.
1919	P 3	Kesteven, Hereward Leighton, M.D., Ch.M., D.Sc., Bulladelah, New South Wales.
1896		King, Kelso, Sir, K.B., Mercantile Mutual Building, 117 Pitt-street, Sydney.
1923		Kinghorn, James Roy, Australian Museum, Sydney.
1920		Kirchner, William John, B.Sc., "Wanawong," Thornleigh-road, Beecroft.
1919		Kirk, Robert Newby, 25 O'Connell-street.
1877		Knox, Edward W., 'Rona,' Bellevue Hill, Double Bay.
1924		Leech, Thomas David James, B.Sc., *Syd.*, 'Orontes,' Clarke-st., Granville.
1920		Le Souef, Albert Sherbourne, Taronga Park, Mosman.
1916		L'Estrange, Walter William, 7 Church-street, Ashfield.
1909		Leverrier, Frank, B.A., B.Sc., K.C., Wentworth Road, Vaucluse.
1883		Lingen, J. T., M.A. *Cantab.*, K.C., c/o Union Club, Bligh-st.

Elected		
1929	P 3	Lions, Francis, B.Sc., Ph.D., Lecturer in Organic Chemistry in the University of Sydney, p.r., 21 Bridge-street, Epping.
1906		Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street.
1924		Love, David Horace, Beauchamp Avenue, Chatswood.
1927		Love, William Henry, B.Sc., "Lumeah," 9 Miller-street, Haberfield.
1884		MacCormick, Sir Alexander, K.C.M.G., M.D., C.M. *Edin.*, M.R.C.S. *Eng.*, 185 Macquarie-street.
1930		MacKenzie, William Donald, M.I.Chem.E., A.I.C., Technical Director, Messrs. Lever Bros. Ltd., Balmain.
1921		McDonald, Alexander Hugh Earle, Director of Agriculture, Department of Agriculture, Sydney.
1903		McDonald, Robert, J.P., L.S., Pastoral Chambers, O'Connell-st; p.r. 'Lowlands,' William-street, Double Bay.
1919		McGeachie, Duncan, M.I.M.E., M.I.E *Aust.*, M.I.M.M.*Aust.*, 'Craig Royston,' Toronto, Lake Macquarie.
1906	P 2	McIntosh, Arthur Marshall, 'Moy Lodge,' Hill-st., Roseville.
1891		McKay, R. T., L.S., M.Inst.C.E., Commissioner, Sydney Harbour Trust, Circular Quay.
1927		McMaster, Frederick Duncan, "Dalkeith," Cassilis.
1916		McQuiggin, Harold G., M B., Ch.M., B.Sc., Lecturer and Demonstrator in Physiology in the University of Sydney; p.r. 'Berolyn,' Beaufort-street, Croydon.
1909		Madsen, John Percival Vissing, D.Sc., B.E., Professor of Electrical Engineering in the University of Sydney.
1924		Mance, Frederick Stapleton, Under Secretary for Mines, Mines Department, Sydney; p.r. 'Binbah,' Lucretia Avenue, Longueville.
1880	P 1	Manfred, Edmund C., Belmore-square, Goulburn.
1920	P 1	Mann, Cecil William, 41 Jenkin-street, Chatswood.
1920		Mann, James Elliott Furneaux, Barrister at Law, c/o T. H. Southerden, Esq., Box 1646 J.J., G.P.O., Sydney.
1914		Martin, A. H., Technical College, Sydney.
1929	P 1	Matheson, Alexander James, Teacher, The High School, Dubbo.
1926		Mathews, Hamilton Bartlett, B.A. *Syd.*, Surveyor General of N.S.W., Department of Lands, Sydney.
1912		Meldrum, Henry John, B.A., B.Sc. 'Craig Roy,' Sydney Road, Manly.
1929		Mellor, David Paver, Assistant Lecturer in Inorganic Chemistry in the University of Sydney; p.r. Flat 8, 'Deanville,' Milson-road, Cremorne.
1922		Mills, Arthur Edward, M.B., Ch.M., Dean of the Faculty of Medicine, Professor of Medicine in the University of Sydney; p.r. 143 Macquarie-street.
1928		Micheli, Louis Ivan, Ph.D., Colonial Sugar Refining Co., Pyrmont.
1926		Mitchell, Ernest Marklow, 106 Harrow Road, Rockdale.

Elected.		
1879		Moore, Frederick H., Union Club, Sydney.
1931		Moppett, Warnford, M.D., Ch.M., Cancer Research Department, University of Sydney.
1922	P 17	Morrison, Frank Richard, A.A.C.I., F.C.S., Assistant Chemist, Technological Museum, Sydney; p.r. Brae-st., Waverley.
1924		Morrison, Malcolm, Department of Mines, Sydney.
1879		Mullins, John Lane, M.L.C., M.A. *Syd.*, 'Mount Stewart,' Edgecliff Road, Edgecliff.
1915		Murphy, R. K., Dr. Ing., Chem. Eng., Lecturer in Chemistry, Technical College, Sydney.
1923	P 2	Murray, Jack Keith, B.A., B.Sc.Agr., Principal, Queensland Agricultural College, Gatton, Queensland.
1893	P 4	Nangle, James, O.B.E., F.R.A.S., Superintendent of Technical Education, The Technical College, Sydney; Government Astronomer, The Observatory, Sydney. (President 1920.)
1930	P 1	Naylor, George Francis King, 'Kingsleigh,' Ingleburn, New South Wales.
1924		Nickoll, Harvey, L.R.C.P., L.R.C.S., Barham, via Mudgee, N.S.W.
1891		‡Noble, Edward George, L.S., 8 Louisa Road, Balmain.
1920	P 1	Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Biologist, Dept. of Agriculture. Box 36A, G.P.O., Sydney, p.r. 'Casa Loma,' Shell Cove Road, Neutral Bay. *Hon. Secretary.*
1903		‡Old, Richard, 'Waverton,' Bay Road, North Sydney.
1921		Olding, George Henry, 'Werriwee,' Wright's Road, Drummoyne.
1930		O'Leary William, S.J., Seismologist, St. Ignatius' College, Riverview, Sydney.
1913		Ollé, A. D., F.C.S., 'Kareema,' Charlotte-street, Ashfield.
1928		Osborn, Theodore George Bentley, D.Sc., F.L.S., Professor of Botany in the University of Sydney.
1921	P 3	Osborne, George Davenport, D.Sc., Lecturer and Demonstrator in Geology in the University of Sydney.
1921	P 1	Parkes, Varney, Conjola, South Coast.
1928		Parsons, Stanley William Enos, Analyst and Inspector, N.S.W. Explosive Department, p.r. Shepherd Road, Artarmon.
1920	P 57	Penfold, Arthur Ramon, F.C.S., Curator and Economic Chemist, Technological Museum, Harris-street, Ultimo.
1881		Poate, Frederick, F.R.A.S., L.S., 'Clanfield,' 50 Penkivil-street, Bondi.
1919		Poate, Hugh Raymond Guy, M.B., Ch.M. *Syd.*, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, 225 Macquarie-street.
1896		Pope, Roland James, B.A., *Syd.*, M.D., Ch.M., F.R.C.S. *Edin.*, 185 Macquarie-street.
1921	P 2	Powell, Charles Wilfrid Roberts, A.I.C., c/o Colonial Sugar Refining Co., O'Connell-street.
1918		Powell John, 17 Thurlow-street, Redfern.

Elected		
1927		Price, William Lindsay, B.E., B.Sc., 60 McIntosh-st., Gordon.
1918		Priestley, Henry, M.D., Ch.M., B.Sc., Associate-Professor of Physiology in the University of Sydney.
1893		Purser, Cecil, B.A., M.B., Ch.M. *Syd.*, 185 Macquarie-street.
1929		Pyke, Henry George, Chemical Testing Assistant, N.S.W. Government Tramways; p.r. Bellamy-street, Pennant Hills.
1927		Radcliffe-Brown, Alfred Reginald, M.A., *Cantab.*, M.A., *Adel.*, F.R.A.I., *Cantab.*, c/o. Institute for International Education. 2 West 45th Street, New York City, U.S.A.
1922	P 4	Raggatt, Harold George, B.Sc., "Meru," Epping-av., Epping.
1919	P 3	Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., Lecturer in Physics, Teachers' College, The University, Sydney.
1931		Rayner, Jack Maxwell, Physicist to the Department of Mines, Sydney; p.r, 125 William-street, Granville.
1928		Reidy, Eugene Nicholas, A.S.T.C., Analyst, Department of Mines, Sydney.
1924		Robertson, James R. M., M.D., C.M., F.R.G.S., F.G.S., 'Vanduara,' Ellamang Avenue, Kirribilli.
1928		Ross, Allan Clunies, B.Sc., Colonial Mutual Building, 14 Martin Place, Sydney. (Member from 1915 to 1924.)
1884	P 1	Ross, Chisholm, M.D. *Syd.*, M.B., Ch.M., *Edin.*, 225 Macquarie-st.
1895		Ross, Herbert E., Govt. Savings Bank Building, 14 Castlereagh-street, Sydney.
1925		Roughley, Theodore Cleveland, Zoologist, Technological Museum, Sydney.
1929		Royle, Norman Dawson, M.D., Ch.M. 185 Macquarie-street, Sydney.
1907		Ryder, Charles Dudley, *D. Eng.* (Vienna), Assoc.I.R.S.M,. (L.), Ass.A.C.I., F.C.S., (L.), Public Analyst (by appoint.), "The Astor," Macquarie-street, Sydney.
1922		Sandy, Harold Arthur Montague, 268 George-street.
1920		Sawyer, Basil, B.E., 'Birri Birra,' The Crescent, Vaucluse.
1920		Scammell, Rupert Boswood, B.Sc., *Syd.*, "Storrington," 10 Buena Vista Avenue, Clifton Gardens.
1919		Sear, Walter George Lane, c/o J. Kitchen & Sons, Ingles-st., Port Melbourne.
1923	P 1	Seddon, Herbert Robert, D.V.Sc., Director, Veterinary Research Station, Glenfield.
1918		Sevier, Harry Brown, c/o Lewis Berger and Sons (Aust.) Ltd., Cathcart House, Castlereagh-street.
1924		Shelton, James Peel, M.Sc., B.Sc.Agr., Holland-av., Bellevue Hill.
1927		Shearsby, Alfred James, 152 Bland-street, Haberfield.
1917		Sibley, Samuel Edward, Mount-street, Coogee.
1900		‡Simpson, R. C., Lecturer in Electrical Engineering, Technical College, Sydney.
1922	P 1	Smith, Thomas Hodge, Australian Museum, Sydney.

Elected		
1919		Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
1921		Spencer-Watts, Arthur, 'Araboonoo,' Glebe-street, Randwick.
1917		Spruson, Wilfred Joseph, S.M. Herald Building, Pitt and Hunter-streets, Sydney.
1916		Stephen, Alfred Ernest, F.C.S., c/o Union Club, Bligh-street, Sydney.
1921		Stephen, Henry Montague, B.A., LL.B., c/o Messrs. Maxwell and Boyd, 17 O'Connell-street.
1914		Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., Captain Piper's Road and New South Head Road, Vaucluse.
1920	P 1	Stephens, John Gower, M.B., Royal Prince Alfred Hospital, Camperdown.
1913		Stewart, Alex. Hay, B.E., 'Yunah,' 22 Murray-street, Croydon
1900	P 1	Stewart, J. Douglas, B.V.Sc., M.R.C.V.S., Professor of Veterinary Science in the University of Sydney; p.r. 'Berelle,' Homebush Road, Strathfield. *Vice-President.* (President 1927.)
1909		Stokes, Edward Sutherland, M.B. *Syd.*, F.R.C.P. *Irel.*, Medical Officer, Metropolitan Board of Water Supply and Sewerage, 341 Pitt-street.
1916	P 1	Stone, W. G., Assistant Analyst, Department of Mines, Sydney.
1920		Sulman, Sir John, Kt., Warrung-st., McMahon's Point, North Sydney.
1918		Sundstrom, Carl Gustaf, c/o Federal Match Co., Park Road, Alexandria.
1901	P 13	‡Sussmilch, C. A., F.G.S., F.S.T.C., A.M.I.E.*Aust.*, Principal of the East Sydney Technical College, and Assistant Superintendent of Technical Education. (President 1922). *Hon. Secretary.*
1919		‡Sutherland, George Fife, A.R.C.Sc., *Lond.*, Assistant-Professor in Mechanical Engineering, in the University of Sydney.
1920		Sutton, Harvey, O.B.E., M.D., D.P.H. *Melb*, B.Sc. *Oxon.*, p.r. 'Lynton,' Kent Road, Rose Bay. Professor of Preventive Medicine and Director, Commonwealth Health Dept., University of Sydney.
1926		Tannahill, Robert William, B.Sc. *Syd.*, M.Sc. "Eastwell," 40 Cammaray Avenue, North Sydney.
1915	P 3	Taylor, Harold B., D.Sc., Kenneth-street, Longueville.
1905		‡Taylor, John M., M.A., LL.B. *Syd.*, 'Woonona,' 43 East Crescent-street, McMahon's Point, North Sydney.
1923		Thomas, David, B.E., M.I.M.M., F.G.S., 15 Clifton Avenue, Burwood.
1919		Thorne, Harold Henry, B.A. *Cantab.*, B.Sc. *Syd.*, Lecturer in Mathematics in the University of Sydney; p.r. Rutledge-st., Eastwood.
1916		Tillyard, Robin John, M.A., D.Sc., F.R.S., F.L.S., F.E.S., Chief Commonwealth Entomologist, G.P.O., Box 109, Canberra, F.C.T.
1923		Tindale, Harold, Works Engineer, c/o Australian Gas-Light Co., Mortlake.
1923		Toppin, Richmond Douglas, A.I.C., Box 1454 JJ, G.P.O., Sydney
1879		Trebeck, P. C., c/o Box 367 F., G.P.O., Sydney; p.r. No. 4 Chesterton Flats, Carabella-street, Kirribilli.

Elected		
1925		Tye, Cyrus Willmott Oberon, Director of Development and of the Migration Agreement Executive Committee, Public Works Dept. Building, Sydney; p.r. 19 Muston-street, Mosman.
1890		Vicars, James, M.E., Memb. Intern. Assoc. Testing Materials; Memb. B. S. Guild; Challis House, Martin Place.
1921		Vicars, Robert, Marrickville Woollen Mills, Marrickville.
1892		Vickery, George B., 9th Floor, Barrack House, Barrack-street. Sydney.
1903	P 6	Vonwiller, Oscar U., B.Sc., F.Inst.P., Professor of Physics in the University of Sydney. *Vice-President.* (President 1930.)
1910		Walker, Charles, 'Lynwood,' Terry Road, Ryde.
1910		Walker, Harold Hutchison, Vickery's Chambers, 82 Pitt-st.
1879		Walker, H. O., 'Moora,' Crown-street, Granville.
1919	P1	Walkom, Arthur Bache, D.Sc., Science House, Gloucester and Essex Streets.
1903		Walsh, Fred., J.P., Consul-General for Honduras in Australia and New Zealand; For. Memb. Inst. Patent Agents, London; Patent Attorney Regd. U.S.A.; Memb. Patent Law Assoc., Washington; Regd. Patent Attorn. Comm. of Aust.; Memb. Patent Attorney Exam. Board Aust.; 4th Floor, 16 Barrack House, Barrack-street, Sydney; p.r. 'Walsholme,' Centennial Park, Sydney.
1901		Walton, R. H., F.C.S., 'Flinders,' Martin's Avenue, Bondi.
1913	P 4	Wardlaw, Hy. Sloane Halcro, D.Sc. *Syd.*, Lecturer and Demonstrator in Physiology in the University of Sydney.
1922		Wark, Blair Anderson, V.C., D.S.O., M.I.Q.C., c/o Thompson and Wark, T. & G. Building, Elizabeth-street; p.r. 'Braeside,' Zeta-street, Lane Cove, Sydney.
1921		‡Waterhouse, G. Athol, D.Sc., B.E., F.E.S., 39 Stanhope Road, Killara.
1924		Waterhouse, Leslie Vickery, B.E. *Syd.*, 6th Floor, Wingello House, Angel Place, Sydney.
1919		Waterhouse, Lionel Lawry, B.E. *Syd.*, Lecturer and Demonstrator in Geology in the University of Sydney.
1919	P 3	Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., 'Hazelmere,' Chelmsford Avenue, Roseville.
1876		Watkins, John Leo, B.A. *Cantab.*, M.A. *Syd.*, University Club, Castlereagh-street; p.r. 169 Avoca-street, Randwick.
1910		Watson, James Frederick, M.B., Ch.M., 'Midhurst,' Woollahra.
1911	P 1	Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney. (President, 1925). *Vice-President.*
1920	P 29	Welch, Marcus Baldwin, B.Sc., A.I.C., Economic Botanist, Technological Museum.
1920	P 1	Wellish, Edward Montague, M.A., Associate-Professor in Mathematics in the University of Sydney.
1921		Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney.

Elected		
1881		‡Wesley, W. H., London.
1931		Wheatley, Frederick William, Director of Education, Cranbrook School, Edgecliff.
1922		Whibley, Harry Clement, 39 Moore-street, Leichhardt.
1909	P 3	‡White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teacher's College.
1892	P 2	White, Harold Pogson, F.C.S., Assayer and Analyst, Department of Mines; p.r. 'Quantox,' Park Road, Auburn.
1928		Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., 143 Macquarie-street, Sydney.
1921		Willan, Thomas Lindsay, B.Sc.,
1920		Williams, Harry, A.I.C., c/o Whiddon Bros.' Rosebery Lanolines Pty. Ltd., Arlington Mills, Botany.
1891		Wood, Percy Moore, L.R.C.P. *Lond.*, M.R.C.S. *Eng.*, 'Redcliffe, Liverpool Road, Ashfield.
1906	P 11	Woolnough, Walter George, D.Sc., F.G.S., 'Callabonna,' Park Avenue, Gordon. (President, 1926.)
1916		Wright, George, c/o Farmer & Company, Pitt-street.
1917		Wright, Gilbert, Lecturer and Demonstrator in Agricultural Chemistry in the University of Sydney.
1921		Yates, Guy Carrington, 184 Sussex-street.

Elected

Honorary Members.

Limited to Twenty.

M.—Recipients of the Clarke Medal.

Elected	
1914	Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, London.
1908	Kennedy, Sir Alex. B. W., Kt., LL.D., D. Eng., F.R.S., Emeritus Professor of Engineering in University College, London, 17 Victoria-street, Westminster, London S.W.
1931	Lyle, Sir Thomas Ranken, K.B., C.B.E., M.A., D.Sc., F.R.S., "Lisbuoy," Irving Road, Toorak, Melbourne.
1915	Maitland, Andrew Gibb, F.G.S., Ex-Government Geologist of Western Australia, 'Bon Accord,' 28 Melville Terrace, South Perth, W.A.
1912	Martin, C. J., C.M.G., D.Sc., F.R.S., Director of Animal Nutrition, C.S. and I.R. University of Adelaide.
1930	Masson, Sir David Orme, K.B.E., M A., D.Sc., LL.D., 14 William-street, South Yarra, Victoria.
1928	Smith, Grafton Elliott, M.A., M.D., F.R.S., F.R.C.P., Professor of Anatomy in the University College, London.
1915	Thomson, Sir J. J., O.M., D.Sc., F.R.S., Nobel Laureate, Master of Trinity College, Cambridge, England.
1921	Threlfall, Sir Richard, C.B.E., M.A., F.R.S., lately Professor of Physics in the University of Sydney, 'Oakhurst, Church Road, Edgbaston, Birmingham, England.
1922	Wilson, James T., M.B., Ch.M. *Edin.*, F.R.S., Professor of Anatomy in the University of Cambridge, England. 31 Grange Road, Cambridge, England.

Obituary 1931-32

Ordinary Members.

Elected.	
1922	Grant, Robert
1877	Hamlet, William Mogford
1914	Reid, David
1919	Stroud, Sydney Harnett

AWARDS OF THE CLARKE MEDAL.

Established in memory of
The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.
Vice-President from 1866 *to* 1878.

To be awarded from time to time for meritorious contributions to the Geology, Mineralogy, or Natural History of Australia. The prefix * indicates the decease of the recipient.

Awarded
1878 *Professor Sir Richard Owen, K.C.B., F.R.S.
1879 *George Bentham, C.M.G., F.R.S.
1880 *Professor Thos. Huxley, F.R.S.
1881 *Professor F. M'Coy, F.R.S., F.G.S.
1882 *Professor James Dwight Dana, LL.D.
1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.
1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
1886 *Professor L. G. De Koninck, M.D.
1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.
1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc. D., F.R.S., F.L.S.
1893 *Professor Ralph Tate, F.L.S., F.G.S.
1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
1895 *Robert Etheridge, Jnr.
1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
1900 *Sir John Murray, K.C.B., LL.D., Sc. D., F.R.S.
1901 *Edward John Eyre.
1902 *F. Manson Bailey, C.M.G., F.L.S.
1903 *Alfred William Howitt, D.Sc., F.G.S.
1907 Walter Howchin, F.G.S., University of Adelaide.
1909 Dr. Walter E. Roth, B.A., Pomeroon River, British Guiana, South America.
1912 *W. H. Twelvetrees, F.G.S.
1914 A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History) London.
1915 *Professor W. A. Haswell, M.A., D.Sc., F.R.S.
1917 Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., B.A., D.Sc., F.R.S., F.G.S., The University, Sydney.
1918 Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
1920 *Joseph Edmund Carne, F.G.S.
1921 *Joseph James Fletcher, M.A., B.Sc.,
1922 Richard Thomas Baker, The Crescent, Cheltenham.
1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
1925 *Charles Hedley, F.L.S.
1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
1928 Ernest C. Andrews, B.A., F.G.S., Government Geologist, Depart- of Mines Sydney.
1929 Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.
1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.
1931 Robin John Tillyard, M.A., D.Sc., F.R.S., F.L.S., F.E.S., Chief Commonwealth Entomologist, Canberra, F.C.T.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.

1882 John Fraser, B.A., West Maitland, for paper entitled 'The Aborigines of New South Wales.'

1882 Andrew Ross, M.D., Molong, for paper entitled 'Influence of the Australian climate and pastures upon the growth of wool.'

The Society's Bronze Medal and £25.

1884 W. E. Abbott, Wingen, for paper entitled 'Water supply in the Interior of New South Wales.'

1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled 'The Tin deposits of New South Wales.'

1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled 'Origin and mode of occurrence of gold-bearing veins and of the associated Minerals.'

1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled 'The Anatomy and Life-history of Mollusca peculiar to Australia.'

1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled 'List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood.'

1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled 'The Australian Aborigines.'

1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled 'The Microscopic Structure of Australian Rocks.'

1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled 'The effect which settlement in Australia has produced upon Indigenous Vegetation.'

1894 J. V. De Coque, Sydney, for paper entitled the 'Timbers of New South Wales.'

1894 R. H. Mathews, L.S., Parramatta, for paper entitled 'The Aboriginal Rock Carvings and Paintings in New South Wales.'

1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled 'The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*).'

1896 Rev. J. Milne Curran, Sydney, for paper entitled 'The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found.'

AWARDS OF THE WALTER BURFITT PRIZE.

MONEY AND MEDAL.

Money Prize of £50.

Established as the result of a generous gift to the Society by Dr. W. F. Burfitt, B.A., M.B., Ch.M., B.Sc., of Sydney. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past three years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded

1929 Norman Dawson Royle, M.D., Ch M., 185 Macquarie-st., Sydney.

VOL. LXV. PART I.

JOURNAL

AND

PROCEEDINGS

OF THE

ROYAL SOCIETY

OF

NEW SOUTH WALES

FOR

1931

(INCORPORATED 1881.)

PART I. (pp. 1 to 144)

OF

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(Plates I - VI.)

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1931.

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VOLUME LXV.

Part I.

PRESIDENTIAL ADDRESS

By Professor O. U. Vonwiller, B.Sc., F.Inst.P.

(Delivered to the Royal Society of New South Wales, May 6, 1931.)

Part I.

It is fitting that I should commence my address with a reference to three noteworthy features of to-night's meeting; it is the first meeting of the Royal Society in its new home, it is the five hundredth general meeting of the Society, and it marks the commencement of the seventy-fifth year of its existence as the Royal Society of New South Wales.

The scientific community of this state is to be congratulated in acquiring Science House, a single building in which we hope that soon nearly all the societies concerned with science and its applications will have their headquarters. The mutual advantages of the increased facilities for co-operation and consultation are obvious, and we may look confidently for increased interest and efficiency in our work, and added achievement and usefulness. I take this opportunity of expressing on behalf of our members grateful appreciation of the efforts of all those who have contributed towards the establishment of Science House.

The history of this movement starts at the annual meeting of the Royal Society of New South Wales on 7th May, 1890, when the retiring President, Professor A. L. Liversidge, in the Anniversary Address, said that it

had long been his desire to see the Society provided with more suitable accommodation. In fact, that what was wanted was a modest edition of Burlington House, Piccadilly, which had been built by the Imperial Government to lodge learned societies. He believed that if the building were carried out even as a commercial undertaking it would prove a very useful investment.

In 1895 vacant land adjoining the Society's house was purchased, Professors Liversidge and David acting for the Society, and additions to the House were completed the following year.

In 1905 the matter of providing a home for the various scientific societies was again discussed and referred to a committee which included Professor Liversidge and Messrs. T. H. Houghton, G. H. Knibbs, and J. H. Maiden. As a result of their labours the House was enlarged, and the Engineering Association of N.S.W. and the Institute of Architects rented rooms in it, being followed shortly after by the Institution of Surveyors and the Dental Association of N.S.W.

The question of new premises was raised in 1914, when negotiations were entered for the purchase of a site and plans for a commodious building were prepared by Messrs. Ross and Rowe. No definite steps were taken during the war, but in the years that followed the matter of enlarging the Society's House and of erecting a new building were frequently discussed and proposals connected with it were brought before the Society by Mr. T. H. Houghton in 1918 and by Mr. A. B. Hector in 1919.

In 1920 Mr. H. C. Kent was appointed Honorary Architect and he prepared plans for extensions to the Royal Society's House, which were carried out in part in 1922, when a number of other societies became tenants.

Among those who urged strongly the building of a Science House at about this time was His Excellency the Governor of New South Wales, Sir Walter Davidson.

Following the appointment of a committee of the Royal Society to report on the question of rebuilding, an invitation was sent in June, 1925, to the Linnean Society of New South Wales to appoint representatives to a joint committee, and in November, 1925, other societies were approached to ascertain which would give financial assistance in the movement. As a result there was formed an Executive Committee of representatives of the Royal Society, the Linnean Society, and the Institution of Engineers of Australia, consisting of Mr. R. H. Cambage, Drs. H. G. Chapman, A. B. Walkom, G. A. Waterhouse, Sir George Julius, and Mr. W. J. Newbigin. This committee approached the Government in March, 1926, with a view to asking assistance in the shape of a site for the erection of Science House. After lengthy negotiation and inspection of many sites a letter was received from the Premier (Hon. J. T. Lang) on 28th July, 1927, stating that the land on which Science House has now been erected would be granted. This action was endorsed by the succeeding Government and the Science House (Grant) Act was passed on 16th June, 1928. Valuable assistance was given at this stage by Mr. C. W. Tye.

In the meantime the Society's house, 5 Elizabeth Street, was sold (October, 1927).

With the aid of the Institute of Architects, in 1928, arrangements were made for an architectural competition, the adjudicators being Messrs. Oakeshott, Joseland, and Berry. Their awards were: First prize, Messrs. Peddle, Thorp and Walker; second prize, Mr. L. C. McCredie; third prize, Mr. John Crust.

Some delay occurred owing to difficulty in obtaining agreement to the form of deed of grant of the land, but after many conferences with the Crown Solicitors the deed of grant was executed and the land made available in September, 1929. Tenders were called for the building of Science House, that of Mr. John Grant being accepted in December, 1929, an agreement in respect to partnership in the building between the Royal Society, the Linnean Society and the Institution of Engineers being signed in the same month. The land was handed over on 7th March, 1930, and the building commenced under the supervision of Mr. S. G. Thorp.

On 24th June, 1930, the foundation stone was laid by His Excellency Sir Philip Game, and to-morrow (7th May, 1931) His Excellency has consented to declare the building open.

That the Royal Society was able to take the share it has in the financial responsibility of the undertaking is due to the excellent management of its affairs, especially in recent years. In this connection we are particularly indebted to our Honorary Treasurer, Dr. H. G. Chapman, for the extraordinarily able way in which he has conducted the financial side of our Society. We are indebted to him, too, for the effective part he took in the negotiations before and after the granting of the site.

The partnership between the three societies made the undertaking possible, because of the greatly increased resources, but at the same time it introduced many great difficulties because of the different points of view on many vital questions. That these difficulties were overcome is due to the determination to achieve their objective on the part of the committee of management appointed by the three societies to co-operate with architect and builder

during the erection of the House and to conduct it when erected. Our gratitude is due to the members of that committee and especially to the representatives of this Society, Dr. H. G. Chapman and Mr. C. A. Sussmilch, who, in addition to acting on that committee, have been responsible for the work of installing the Society in its new home early this year.

For the efforts of those mentioned and of many others we owe our thanks. It is for us and our successors to justify those efforts by making the Royal Society of New South Wales worthy of its name, its history and its home.

That we can celebrate our five hundredth meeting and our seventy-fifth birthday is evidence that the Society has been of value to the community; otherwise it could not have lived so long. During its long life, the Society, which under other names has existed for a period much greater than seventy-five years, has enjoyed varying fortunes; to-day, in common with the rest of the country, it is experiencing difficulties of an abnormal kind. While we may hope that the advantages of our new situation will compensate some of these, I feel that the time has come when we must review our position in view of altered conditions, and, if necessary, make changes, perhaps radical changes, in our methods, if we are to maintain our position and extend our influence and usefulness.

Thirty-six years ago, during a year of bad times, our membership fell from 445 to 420. During the past year it has fallen from 324 to 307. When we consider the change in the population of New South Wales during this period, a bad state of affairs is suggested, though I wish at once to point out that the figures do not necessarily indicate a falling off in the interest in science or in the quality of the work done by our Society. During the

last generation there have been formed many new scientific societies of varying degrees of importance, and mostly of highly specialised interests; one inevitable result is a fall in our membership, especially in times like these.

It is, I think, a matter of the greatest importance that we should take steps to maintain and to improve the position our Society holds, not for the sentimental reasons which are real enough among the older among us, but because it is very necessary that, besides the various specialised bodies, there should be one like ours where workers of all branches may meet, may know one another, and learn of the work of one another.

The library of the Royal Society, now adequately displayed for the first time, gives one good reason for making a special effort to improve the position of the Society. It is one of the best scientific libraries in Australia, and is available to all qualified to use it, whether members are not. Its growth depends largely on exchanges with other institutions, and our success in establishing these must depend on the value and variety of the papers in our proceedings, while, of course, our ability to purchase new works is limited with our income.

A further reason for the existence of a truly representative and authoritative society is that it may well form a channel through which scientific workers may offer their assistance to the state and through which the state may ask such assistance. At present, from time to time individuals among us are asked for help in connection with special problems, but the possibilities of such help are not realised as much as they might be. A Royal Society such as one would like this to be might do much in showing the people and their representatives the possibilities, and the limitations, of scientific endeavour.

That we cannot do all this at present is due partly to our lack of numerical strength, but mainly because certain sections of science are not represented adequately among our members. I feel that we must take steps to add to our numbers many who are now unable to join us either because we exclude them or because of financial considerations. This means constitutional changes not lightly to be made and a further development of our existing machinery for promoting sections specialising in various branches.

The changes I have indicated must be made only after long consideration. That is one reason why no definite steps were taken last year; another is that the financial uncertainty accompanying the changed condition of the Society rendered it unwise to take any step likely to cause financial embarrassment even of a temporary nature.

These matters will, I trust, receive further consideration, and I hope that it will soon be possible to invite applications for membership, if not full, at least associate, from all with good scientific qualifications, with a subscription rate which will be within the reach of the junior and poorly-paid scientific worker.

For the suggestions made here I alone am responsible; though some of my views have been mentioned to members of the Council, that body has not been invited to discuss them and has not yet been asked to express an opinion on them.

The Annual Report shows that, in spite of adverse conditions, the meetings of the Society maintained the standard of past years in the quality and number of papers submitted, and in the attendance of members. Measures taken during the year to make the monthly meetings of greater general interest to members have had encouraging

results, and it is hoped that, guided by last year's experience, further improvement will take place in the coming year.

I record with pleasure that Mr. E. C. Andrews has been awarded the Lyell Medal by the London Geological Society.

The Maiden Memorial Pavilion was opened on 20th May, 1930, by His Excellency Sir William Cullen, Lieutenant-Governor of New South Wales.

This year, the first Liversidge Memorial Lecture under the auspices of this Society will be delivered.

OBITUARY.

Charles Chilton, M.A., D.Sc., M.B., Ch.M., was born in England in 1860 and was taken to New Zealand as a child. In Canterbury College he studied natural science and graduated with honours in zoology. After spending fifteen years as a schoolmaster with marked success, he left New Zealand and entered as a medical student at Edinburgh, where he had a distinguished course, followed by post-graduate work on diseases of the eye in England and the Continent. Returning to New Zealand, he practised in Christchurch as an ophthalmic surgeon, but at the same time devoted all his spare time to Zoology, publishing a series of important papers on the *Crustacea*. When Professor Dendy went to King's College, London, Dr. Chilton, who was acting professor in his absence, was appointed to the chair of biology at Christchurch.

He made a mark both as teacher and research worker, and also as administrator. Most of his published papers refer to the Crustacea, in which group he specialised. He

gave a good deal of attention to the fauna of subterranean waters and published a valuable memoir on the subterranean crustacea of New Zealand. In 1907 he took part in an expedition to the sub-Antarctic islands of New Zealand, and afterwards edited the volumes recording the scientific results. He was responsible for the establishment of the mountain biological station at Cass for the investigation of New Zealand alpine fauna and flora.

Professor Chilton, who was elected an honorary member of the Royal Society of New South Wales in 1918, became rector of Canterbury College in 1921, which position he held until 1927, when ill-health forced him to resign. He died on 25th October, 1929.

Sir William Turner Thistleton-Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., was born in London in 1843. In 1861 he entered King's College with a view to qualifying in Medicine, but before completing his course, entered at Christchurch, Oxford, and graduated there in mathematics. At Oxford he became a keen student of botany, and, after leaving, occupied chairs in natural history and botany in quick succession at Cirencester, Dublin, and London. In London he came into touch with Sir James Hooker, Director at Kew, who had him appointed Assistant Director in 1875. At this period, with Huxley at the Royal College of Science, Thistleton-Dyer developed practical courses in botany—then for the first time a laboratory subject—his work being practically the starting-point of the modern scientific treatment of botany in Great Britain.

At Kew he realised the possibilities of the imperial function of the institution and kept the various botanical establishments of the Empire in close touch with it, stimulating everywhere botanical exploration and collec-

tion and the exchange and cultivation of useful plants. In 1885 he succeeded Hooker in the directorship, occupying this position until he retired in 1905. He was elected an honorary member of the Royal Society of New South Wales in 1900. After his retirement he devoted himself to the pursuit of classical studies and wrote several critical papers on the subject of plant names in the classics. He died on 28th December, 1928.

Joseph Eldred Bishop was born in Victoria in 1864 and came to Sydney as a newspaper representative in 1892. Later he became, in succession, secretary, manager and proprietor of West's Wheel Works and occupied a prominent place in a number of business associations and in various local movements. Elected a member of the Royal Society of New South Wales in 1920, he was a regular attendant at meetings, and in 1921 became chairman of the Industrial Section. He was actively interested in social, economic and political questions, and was a contributor to the Economics Section of the Australasian Association for the Advancement of Science, being also the writer of numerous articles in the press. He was a foundation member and Vice-President of the Economic Society of New South Wales. His death took place on 1st May, 1930.

Robert Lionel Faithfull, L.R.C.P., M.D., New York, L.S.A., London, was a member of one of the oldest families in the State. He was a son of the late William Pitt Faithfull and was born on 27th July, 1853. He studied Medicine in Sydney and in the United States. For more than thirty years he practised in Sydney, and during late years occupied a prominent place in business affairs, being director of a number of important commercial institutions.

A man of quiet disposition, he enjoyed the high respect of his colleagues. He became a member of this Society in 1887, and though in recent years he seldom attended meetings, he retained his interest in its activities. He died at Moss Vale on 8th June, 1930.

Joseph Palmer was born in London in 1841 and came to Australia with his parents in 1853. After serving as clerk to Mr. Josiah Mullens, a sharebroker, for nine years, he commenced business on his own account in 1872 and was one of the first members of the then newly-formed Sydney Stock Exchange, of which he was at one time chairman. From boyhood he was keenly interested in religious matters and was an active worker in connection with the New South Wales Bush Missionary Society, the Y.M.C.A., and the Baptist Church. He published several books and many pamphlets on religious questions which received considerable attention. He was elected a member of this Society in 1880 and for a long time took an active interest in its proceedings. His death occurred on 7th May, 1930.

Joseph Thompson, M.A., LL.B., was born in Sydney 84 years ago. He attended the Sydney Grammar School (his name is the first on the list of pupils of that school), and, proceeding to the University of Sydney, graduated there as M.A. and LL.B. He read with the late Sir Edmund Barton and was admitted as a solicitor in December, 1871. He worked at his profession to within a few days of his death, and was one of the oldest solicitors practising in Sydney. He became a member of this Society in 1913. His death occurred on 28th October, 1930.

Before passing to the second part of my address, I wish to make further brief reference to the question of what part the scientist should take in the present state of

national and world affairs, and in particular to the suggestion, made in more quarters than one, that this is no time for investigations in pure science for its own sake, but that we should concentrate our efforts on solving the acute practical problems of the day. This view is illustrated by a cable message appearing in our press at the time of the last meeting of the British Association for the Advancement of Science. It was:

> There are no outstanding papers. Indeed, many of the papers seem particularly futile in view of the gravity of the times in which men live. The minds of scientists are apparently not concentrated on the larger issues.
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> A young Cambridge professor propounded a new theory of the atom, which the scientists present confessed they were unable to understand. The author declined to put his theory in more simple language for fear of being inaccurate.
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> —"Sydney Morning Herald," 10th September, 1930.

I would point out that the criticism in this cable is not constructive; it does not indicate clearly what work the scientists should do in place of carrying out those investigations for which, presumably, they were well qualified. That chemists and physicists should try to devise schemes for the economic conduct of the country would hardly be profitable; their suggestions would probably be nearly as crude and futile as those so freely produced in parliament and press these days. In particular what should this young Cambridge professor do? Perhaps if he devoted himself to industry he might prove a brilliant success and invent labour-saving methods, with the immediate result of increasing greatly the number of unemployed; on the other hand, his achievement in such a field might well be negligible.

During the war, men of science proved themselves as adaptable and resourceful in invention as they had been

in research. Eminent chemists, mathematicians, physicists, geologists, biologists, worked on definite problems, and, thanks to their experience and training and to the unstinted expenditure on necessary equipment and apparatus, they achieved brilliant success in many instances; but to-day, unless problems are submitted for which the scientist's training specially equips him, and unless the necessary material assistance is provided for the attack on these problems, I do not see that he can do better than devote himself to that pursuit of knowledge which is the life of the true scientist and, incidentally, the foundation of all the advances which have benefited mankind in the past. The only futility I can see in the action of the Cambridge professor is the verbal delivery of a paper on a subject of extraordinary difficulty, understanding of which can come only after repeated reading and close study of the printed account. In a year in which centenaries connected with Michael Faraday and with Clerk Maxwell are celebrated it should be unnecessary to attempt to justify the pursuit of knowledge for its own sake.

While maintaining that all encouragement should be given to pure research, I can quite consistently urge that the State should use trained scientists to a greater extent in solving the many problems for which their knowledge and training equip them; that we should, on the one hand, try to let the scientist realise that he can assist in some of these, and, on the other, make our men of affairs understand what the scientist might do, given adequate time and material. As I stated earlier, a society such as ours might do particularly valuable work in imparting this knowledge of what is wanted and of what might be done.

Part II.

A GENERATION OF ELECTRON THEORY.

Introduction.

In the second part of my address I feel that no apology is needed for a discussion of points of purely scientific interest. The selection of subject was suggested by an examination of past presidential addresses in which, for one delivered by a physicist, I had to go back thirty-six years to 1st May, 1895, when Professor Threlfall (now Sir Richard Threlfall) gave the anniversary address of this society. The perusal of that address reminds one at once of the vast increase in knowledge in physics gained since that day, and, at the same time, of the yet more remarkable changes in the attitude or viewpoint of the physicist. In that address a tribute is paid to three eminent German physicists who died not long before—Helmholtz, Hertz and Kundt. The recollection of the work of these men, together with the account of contemporary physical research given in that address, including a discussion on many investigations on electric oscillations and waves following the work of Hertz, reference to the beautiful application of wave theory of light to colour photography by Lippman and by Wiener, to much work on exact measurement of electrical properties of materials, and, as the crowning item, the discovery of argon by the late Lord Rayleigh, makes us realise that the curtain had not yet risen on what Lord Rutherford calls the heroic age of physics, the beginning of this generation of tremendous and sensational advance of knowledge and ideas.

The following quotation from that address, referring to the discovery of argon, is of interest, the first part indicating the knowledge and attitude of that time, while

the last part shows an appreciation of facts of which we might well be reminded to-day:—

"It appears to be a singularly inert gas, (to which property it owes its late discovery), heavier than nitrogen, and most probably an element, since there is strong evidence that it is monatomic. Should this be the case, room will have to be made for it in Mendelejeffs' series,—one can only pray that it may fit a vacant place and not turn the whole of chemistry upside down by refusing to come in under the periodic law. It would come in if its atomic weight were twenty, but the discoverers think it is forty. However, out of such catastrophes, advances are apt to be made, and if we have to mend our periodic law we shall probably get something better in its place, perhaps some light on the dynamics underlying it. I cannot close this brief notice without directing your attention to the magnificent triumph which this discovery has obtained for the method of enquiry by means of prolonged, laborious, and exact measurement, as opposed to the method of happy inspiration. Contrary to the popular idea, the vast majority of discoveries have been made by the methods employed by Lord Rayleigh, of which the essence is that no obscurity, however small, is to be passed over until it is completely sifted."

That address, however, was given only just before the first announcements of the remarkable discoveries which introduced the new era. Within a few months Röntgen discovered X-rays; in the following year Becquerel published an account of the first observations of radioactivity, while already J. J. Thomson and his students were engaged in the researches which, during the years immediately following, gave fundamental facts concerning the electron. During the next generation, as all know, we have had a succession of remarkable discoveries and an extraordinary growth of knowledge concerning atoms and atomic processes. With all the newly-discovered phenomena relating to atomic structure, electricity and light, we find electrons intimately associated, and all the new hypotheses and theories are closely bound with views as to the nature and behaviour of electrons, so that, as the last physics

address before this society was delivered just before the discovery of the electron, it seemed appropriate that in this one, given a generation later, I should review some phases of the advances in knowledge and changes in ideas following from that discovery.

Remarkable as have been the discoveries made during the last thirty-six years, I think that their significance in the history of physics will depend most of all on the extraordinary developments in the philosophy of the physicist, in the changes which have taken place in our statement of the fundamental principles in terms of which we describe the phenomena of nature, and it is to some of those that I wish particularly to address myself.

Thirty-six years ago certain fundamental principles were apparently completely and convincingly established. Newtonian mechanics, Maxwell's theory, and the principle of conservation of energy formed a foundation concerning which generally there were no doubts. In optics the idea of waves in an aether seemed adequately and uniquely to meet all the evidence, and Hertz's experiments had confirmed Maxwell's views as to these light waves being electric waves. Additional generalisations such as the second law of thermodynamics helped to give a generally satisfactory picture. Of course, there were innumerable difficulties and perplexities, and the physicists of that day were under no illusions as to the approaching completeness of their knowledge, but in general it was felt that future experiments and discovery would give solutions to these in terms of developments of the accepted theories, involving no radical changes in underlying ideas.

The outstanding feature in the philosophy of the physicist of that period was, perhaps, the deterministic outlook. Generally it was tacitly believed that a sufficiently

full knowledge of the universe was conceivable to enable a being with adequate mathematical skill to predict the course of events in the future, and to recall the past. Such knowledge would involve a statement of the position and momentum of each particle of matter at a given instant, and of the various physical laws describing the phenomena of nature. While it was recognised that we could never attain absolute accuracy of measurement, so that the necessary knowledge could not be obtained, the success which the physicist met in his constant endeavour to improve his measuring devices and his skill in using them, in his aspirations towards the extra place of decimals, which is one of the most important factors in the growth of knowledge, encouraged the belief that the future would lead to ever closer and closer approximation to absolutely precise determinations, and that with this we should be able more and more correctly to give the history, past and future, of each body in the universe.

The arguments of the philosophers who made suggestions that this was fundamentally wrong, that there was doubt as to the correctness of the accepted principles of the physicist, were esoteric; physicists, even the most eminent, generally were not in the inner circle which heard and understood these.

With the growth of our knowledge of atomic physics it has been necessary from time to time to introduce novel general principles, supplementing those hitherto sufficient, and later modifying some of these so that they are only special cases of greater generalisations, while during recent years there have taken place changes of a more profound nature, especially in connection with the deterministic view, the significance of which it is difficult to-day to assess, though there can be no doubt as to their importance and interest to both philosopher and physicist.

The Beginning of Electron Theory.

The idea of a fundamental electric charge, an "atom of electricity," is quite old. The atomic theory of Dalton, combined with Faraday's laws of electrolysis, indicates clearly the existence of such unit charge, and the name "electron" was suggested for this hypothetical electric atom by Johnston Stoney some years before its isolation. The early history is well known; electrons separated from atoms were found in connection with electric discharge in gases, radio-activity, the photo-electric effect, emission from incandescent solids, all with the same charge and the same mass, while the Zeeman effect was interpreted to mean that within atoms there were also electrons of the same nature. The assumption that the mass was wholly electrical in nature, borne out by the discovery that the mass was not constant but depended on the velocity, led to an estimate of the actual size of the electron, which, for a long time, was visualised as a tiny sphere of negative electricity of quite definite size, though there were suggestions of it being a disc or a ring.

There can be no question as to the sensational character of the discovery, within a few years, of X-rays, radio-activity and the electron. Light was at once thrown on diverse phenomena in physics and chemistry, and many facts concerned with heat, light, elasticity, electricity, magnetism, chemical combination, the periodic law, were reconciled, at least qualitatively, with the new electron views. At the same time, while a new world of investigation was opened, at first there was no reason to suggest anything fundamentally wrong in the accepted bases of physics; it was generally felt that all the new and varied phenomena would be found eventually to fit in with the then accepted principles, though it is true that there were those who insisted that laws based exclusively on observations on

matter on relatively large scale must not be considered necessarily to hold when dealing with particles of atomic or sub-atomic dimensions.

In the theory of relativity, which in its simplest and special form was enunciated early in this century, and in Planck's quantum theory, advanced to reconcile the facts of full radiation at about the same time, we have the first suggestions of radical changes in accepted views; but both these theories, especially the latter, did not receive general attention when first stated, several years elapsing before their significance was realised. One of the earliest applications of the theory of relativity was to the question of the relation between mass and velocity of an electron; the close agreement between prediction and observation was a triumph for the theory and at the same time strengthened the view that the picture formed of the electron was essentially correct.

Theories of X-rays.

An interesting phase in the development of our ideas is the controversy regarding the nature of X-rays in the early years of this century. Though apparently ended in 1912, it is, I think, worthy of notice in view of recent developments. Practically from the time of their discovery the commonly accepted view of X-rays was that they were a kind of light of very short wave-length, though for a long time there was no convincing proof of this. Undoubtedly there were difficulties in the wave theory, and Sir J. J. Thomson at quite an early stage made what appeared a far-fetched and rather unconvincing picture of the "spotted wave front" to remove these. This is notable because he introduced the idea of the energy being localised at certain points on the wave front instead of being distributed continuously as in the then accepted view of light waves.

Based on a study of the secondary effects produced by X-rays, Sir William Bragg advanced an alternative theory which, though put on one side after a few years, attracted a lot of attention at the time and is interesting to-day because it involved certain ideas greatly resembling those now accepted. This was the neutral pair theory, according to which X-rays consisted of a doublet, a negative and a positive electron, the latter having a negligible mass. The interaction between matter and such a doublet might result in the detachment of the positive, the negative going off as a free electron with the same energy as the original doublet; this free electron, meeting matter again, might pick up a positive, an X-ray similar to the original one being so produced. Bragg showed that the various phenomena of X-rays, their great penetrating power, absence of deflection in magnetic and electric fields, polarisation on reflection, secondary effects, all fitted in with his theory, at least as well as with the wave theory. It is interesting to see how each experimental fact advanced to disprove his theory was shown by him to be consistent with it and, in a number of cases, to favour it against the other.

In 1912 the discovery of diffraction effects of X-rays seemed definitely to settle the question; at least it showed that X-rays were light rays, and, as is well known, Bragg himself developed this line of attack, becoming the recognised leader in using interference effects with X-rays as a means of investigating the arrangement of atoms in crystals. We have to remember that the generally accepted view of light in 1912 is by no means the same as that of the present day, and while Bragg's hypothesis then seemed quite wrong, it actually has important features in common with those of to-day. The idea of the change from one form to another, X-ray to electron to X-ray, the energy being constant, we accept to-day though we do not admit

his picture of the X-ray—not that we have any picture to substitute for it. Of course, one important point of divergence is that on his view the speed of the X-ray is less than that of light. A particularly interesting point to recall is the admission that there must be a wave associated with the formation of the X-ray, there being produced together the doublet and an aether wave, the latter being of negligible energy. This suggestion of duality, corpuscle and wave, is notable when we consider the present-day views. One point in particular we might note here, one illustrated time after time, namely, that more than one picture might be made to fit the observations; that we can form only one picture consistent with all the known facts is no proof that it is correct. This is not a new idea; many years ago Clerk Maxwell pointed out that an infinity of hidden mechanisms can be imagined, all of which will produce a given motion of the observable parts of a dynamical system; but I think that the appreciation of this is far more general to-day than even a few years ago. One important difference in the attitudes of the physicist of to-day and of the past is in the picture made of physical processes; to-day such a picture possesses no value except its convenience; it may afford a suitable method of stating the laws of some phenomenon, simpler than or supplementing, mathematical expression, and suggesting further developments. Often in the past such pictures were regarded as very real presentments.

By 1912 Planck's quantum hypothesis had gained ground, receiving support through its application to the question of the variation with temperature of specific heats and particularly through Einstein showing that the facts of photo-electricity were quantitatively consistent with it; these facts seemed definitely to show that the energy in

light waves was localised, not distributed in a continuous manner over the wave surface, and so introduced the outstanding difficulty of modern physics, the double nature of light, sometimes apparently inevitably undulatory, at others equally inevitably corpuscular. At this time there was not a general realisation of the fact that the quantum theory, applied to X-rays and γ-rays, would reconcile the various facts of the secondary effects of these radiations, otherwise the decision that they were of the same nature as light might have been made earlier. That it was not, is, however, not surprising, because at the time only those aspects of X-rays demanding a corpuscular interpretation were prominent; it was after diffraction effects were noted that the same duality and the same difficulties were found with both light and X-rays.

In 1913 the wave theory of X-rays was well established, or rather the fact that many phenomena connected with X-rays as with light seemed to demand a wave theory, and the work of Rutherford on scattering of α particles and that of Moseley on characteristic X-rays established the nuclear theory of the atom, giving a picture of the counterpart of the electron, the proton, an entity with positive charge equal to the negative charge on the electron, a mass about 1840 times as great and a radius as many times smaller if classical theory could be applied to such cases. Moseley's work, it will be remembered, established the importance of the atomic number, solving the difficulty of the atomic weight of argon being 40—the "catastrophe" of 1895.

The Bohr Atom.

In this year came one of the most notable advances, Bohr's theory of the hydrogen atom, giving a picture of the atom and a statement of the processes of light emission consistent to the highest precision obtainable with the

observed facts of the spectrum of atomic hydrogen, a theory notable because it introduced new extensions, limitations, and qualifications to the classical electro-magnetic theory, namely, the restriction of the electronic orbits, possible on the old theory, to these satisfying certain quantum conditions, and the assumption that an electron in such orbit is non-radiating, whereas on the classical theory it must radiate energy. The essential point of this theory, of course, is the idea that the emission of light accompanies the transition from one of these "stationary states" to another, the frequency of the light being proportional to the change in energy of the atom in accordance with Planck's quantum hypothesis, $W = h\nu$.

The Bohr theory thus introduces new concepts not to be expected from classical theory and in fact at variance from it, though at the same time the picture of the atom is based on classical considerations.

A specially significant feature is the lack of definiteness of statement of the behaviour of an individual atom. For example, if a hydrogen atom is in a state other than those of lowest or second lowest energy, one of a number of transitions might occur. To take a special case: if it is in a state characterised by principal quantum number 5, it might change to any one of states 4, 3, 2, or 1, with the emission of the corresponding light quantum. It may be possible to determine the relative probabilities of the occurrence of these changes so that if we are concerned with a large number,—say a million—of such atoms, the numbers making each of the four possible changes might be predicted and therefore the relative intensities of the four spectral lines; in other words, we have statistical knowledge and can give statistical laws, but concerning the individual atom all that can be given is a statement of the

various changes possible and their relative probabilities. For any so excited atom these probabilities of making spontaneously given changes might be modified by various factors as the presence of fields of force, of radiation of various kinds, but it appears impossible to determine which of several possible changes actually is to take place. This constitutes an important departure from the deterministic view; instead of predicting what will happen, statement can be made only of possible happenings and of the relative probabilities of their occurrence. Of course, it is not obvious that this interpretation must be put on Bohr's theory, but the strong suggestion of indetermination is interesting, inasmuch as it leaves room for the introduction of influences other than those accounted for by the ordinary physical laws, call it the law of chance, divine control, or what you will.

Developed brilliantly by Bohr and many others, the theory achieved remarkable success, which is now common knowledge. The observed facts of the spectra of many elements fitted it, new effects such as the multiplicity of the hydrogen lines were predicted and verified in striking manner. For ten years the theory was accepted as giving a picture of atoms essentially correct, that there are stationary non-radiating states characterised by definite electronic orbits, a spectral line corresponding with the transition from one such state to another, the transition involving an electron changing from one orbit to another or perhaps two or more electrons making such changes simultaneously. The X-ray spectra supported the theory convincingly, while Bohr showed that the facts of the periodic law were well explained with the aid of Pauli's principle that no two electrons in an atom can have the same set of quantum numbers.

The difficulties certainly were great. In the first place, while more or less definite pictures were given of the various stationary states of atoms, it was impossible to visualise the process of transition or to see why and how it should be accompanied by the emission of light of the frequency indicated by Planck's law. Then, while there were many cases of excellent agreement between observation and theory, there were noteworthy inconsistencies; to reconcile some of the frequency relations between certain spectral lines it was necessary to introduce arbitrary modifications and corrections to the quantum numbers such as the addition or subtraction of 1/2, justified often only by their success. It is true that the idea of electron spin helped a lot in connection with the Zeeman effect and multiplicities of lines in certain optical and X-ray spectra, giving in fact remarkable quantitative agreement in many cases, but with wider application the Bohr theory had to be modified more and more seriously, losing the attraction of its original simplicity in the endeavour to make it meet the ever-increasing observations. This has been the fate of many theories in the past; at first a simple statement is adequate, but with attempts to prove its general application it has ever to be made more and more complicated until it is so cumbersome that it breaks down. One recalls Newton's corpuscular theory of light, adequate for the facts of reflection and refraction; the endeavour to reconcile with it what we now call interference effects involved complications such as the introduction of periodicity, giving an air of artificiality which, with the work of Young and Fresnel more than one hundred years later, led to it being discarded, though to-day we can see in it a suggestion of the twofold nature of light which now we are compelled to accept.

That twofold nature of light was emphasised more than ever by Bohr's theory, which gives a picture fitting remarkably well one class of light phenomena, those involving the corpuscular idea, but a picture impossible to reconcile with interference and diffraction effects. It is true that his correspondence principle showed certain approximations between deductions from the classical and the later theory, but this in no way removed the difficulties. More and more clearly was it established that, while the theory of Bohr gave a remarkably accurate method of statement, one consistent with many observational facts and valuable as a means of prediction of new knowledge, its extended success depended on so many and such artificial modifications that it was quite obvious that it was incapable of satisfying all demands made on it, that many phenomena concerning spectra would not fit the theory. No one was more emphatic on this point than Bohr himself, who has taken a prominent part in developing the later ideas now to be discussed.

Wave Mechanics.

The latest stage in our theories commences with de Broglie's postulate of electron waves enunciated seven years ago. There had already been a number of suggestions that the association of an internal frequency with the individual electron would remove certain difficulties in the interpretation of spectra, and the idea of the spinning electron advanced somewhat later was a quantitative application of this used with remarkable success in amplifying the original Bohr theory. De Broglie, by logical development of the ideas of Einstein and Planck, showed that, associated with an electron (and, in fact, with any particle), there should be a frequency proportional to the mass and depending on the velocity, and waves of some kind, the wave length also depending on mass and velocity.

In the case of electrons with velocities met in ordinary observations, the wave lengths calculated are comparable with those of X-rays. On de Broglie's theory the wave is a guide or control of the particle; the changes of motion of an electron are due to modifications of the wave motion, refraction for example, wave mechanics being thus introduced instead of the Newtonian mechanics. Extended mathematically by Schrödinger and others, this wave theory has proved extremely fruitful, producing excellent agreement between theory and observation, and in general bringing order into the almost chaotic hypotheses of atomic behaviour. It introduces many difficulties: the first is the question of the nature of these waves. They are not light waves; their velocity is greater than that of light, being as many times greater than it as the velocity of the particle is less—this being itself a startling view when we recall the impression formed from relativity considerations of the impossibility of a velocity equalling, let alone exceeding, that of light. Then the mechanism by which such rapidly travelling waves guide slowly-moving particles is not easy to visualise. The position is not simplified by the later developments of Schrödinger and others, indicating that generally the waves are not three dimensional but multi-dimensional.

The first difficulty is met by the fact that in a case of wave motion in which the wave velocity depends on the frequency, as it does in the de Broglie waves, the velocity of transport of energy is the group velocity and not the wave velocity. In the case of de Broglie waves the group velocity is readily shown to be the velocity of the particle. De Broglie visualised the electron, associated with which is all the energy, as the centre of a wave group moving with it, modifications of the waves causing changes in the motion of the electron.

This theory does not remove the old difficulty of duality in the phenomena of light; instead it extends it, making it a general principle. At first this duality was met in light in the visible and ultra-violet, then it was apparent in X-rays and γ-rays, and now we have in the electron, and presumably in all matter, in addition to the well-known corpuscular attributes, wave characteristics, though the waves must be essentially different in nature from light waves. In the suggestion that the motion of matter is really controlled by the waves, that to describe it we must formulate the laws of these waves and determine their behaviour, in place of the ordinary method of Newton's laws of motion, we have an absolutely novel idea. Of course, in the case of particles of ordinary matter the waves are extremely short, and it can be shown that here the Newtonian laws give correct results; in the case of electrons the new theory often gives results very different from those of the old theory and, as already stated, more consistent with observed facts.

Applied to the hydrogen atom these new waves fitted well with the stationary states, the orbits of Bohr being orbits which satisfied the condition that stationary matter waves of wave length appropriate to the electron speed in the orbit could be established. For example, in the case of circular orbits in which the electron speed is constant, the orbits must have a length equal to an integral number of wave lengths; the orbits satisfying this "resonance" idea are found to agree excellently with those calculated by Bohr.

The most striking evidence is given by the discovery that with a stream of electrons diffraction or interference effects can be obtained resembling those of γ-rays. Practically all the experiments on reflection and transmission

of X-rays with crystals can be repeated with electrons with similar results. A beam of electrons falling on a crystal is reflected as a number of beams in various definite directions, depending on the grating constant of the crystal, on the angle of incidence and on the speed of the electrons, and the wave lengths indicated by such experiments depend on the velocity exactly as the theory demands. This experiment corresponds with those of Bragg with X-rays; other experiments on the transmission through thin sheets of crystalline matter give patterns suggesting those obtained by Laue with X-rays. Further, just as a ruled diffraction grating has been used in X-ray analysis, so it has with a stream of electrons.

Such results as these might well be taken as affording overwhelming evidence of the objective reality of the waves and of the correctness of the view that they do guide the electrons. However, we must exercise caution in coming to this decision. Here again in the endeavour to make the theory fit in with all the pertinent facts, there has been introduced a succession of extensions and modifications of the original de Broglie idea, each fresh hypothesis in turn having to be discarded or further modified.

At one time the old idea of the electron was abandoned altogether; it was thought that it was the wave group and not what is equivalent to a point in it, that instead of being a tiny particle it had practically infinite extension; but the density of charge being measured by the intensity of the wave, the effective volume was actually very small, but still much greater than that formerly attributed to the electron.

A later idea is that the electron might be as originally visualised, but that from the wave function giving the wave amplitude at each point of space an estimate is

obtained, giving not the actual density of charge there but the probability of the electron being at that point, the chance of the electron being in any particular position being proportional to the wave intensity there.

We have in this last idea, which with important modifications is widely favoured at present, an extension of that notion of indefiniteness already indicated in Bohr's first work. We do not picture the electron in a definite position, but simply state the probability of its being in any place, maintaining that it is possible for it to be elsewhere.

This apparent retrograde step, however, leads to progress, one important achievement being the application of like ideas to α particles, the well-known relation between stability of radio-active atoms and speed of emission of α particles, the Geiger-Nuttall law, being in excellent accord with the demands of this theory.

There are many other triumphs of these new theories; the later difficulties of the original Bohr theory are removed, the facts of the Zeeman effect, the Raman effect are consistent with it, remarkable results such as the existence of two kinds of hydrogen molecule are predicted and verified by absolutely independent methods, good progress is made in obtaining expressions for the relative intensities of lines in spectra, though much remains to be done here both from theoretical and experimental standpoint. One interesting application is indicated which may prove of great value. Electron diffraction gives a method of examining the thin films of gas existing on metal surfaces. Further knowledge of these will undoubtedly assist in the solution of many problems in physical chemistry of scientific and economic importance. However, instead of discussing these, I wish rather to point out some more striking consequences of these latest views.

The Uncertainty or Indetermination Principle.

Perhaps the change in our ideas, fundamentally most important, is that involved in the principle of uncertainty or indetermination enunciated by Heisenberg in 1927, and now widely accepted as an inevitable truth. To appreciate its significance we must recall the deterministic view of a generation ago. Already we have seen that modern theory indicates that when we consider atoms and their constituents we cannot hope to make definite predictions concerning the individual, but that we may try to determine a number of possible changes and the relative chances of the occurrence of these. We have seen, too, that the latest work shows often an indefiniteness in the statement of the position of a particle, that we may be able to say, not where a particle is, but what is the chance of its being at a given point at some particular moment. The principle of indetermination states that both the position and the momentum of a particle cannot be determined with absolute accuracy, that from the nature of things there must be an error or uncertainty in the measurement of one or both these quantities, and further, that the product of the two amounts of uncertainty cannot be less than a definite though small amount, namely, $h/2\pi$. The greater the precision with which one quantity is measured, the greater the inevitable uncertainty in the other. If, for example, the position of an electron could be determined with absolute certainty, the velocity must be absolutely indefinite and *vice versa.* Many examples and illustrations of diverse nature have been given, some more convincing and logical than others, and it is shown that the product of the inevitable uncertainties is always of the order given by this principle.

We get from the principle a co-relation between the electron waves and the electron which indicates a mathe-

matical and not a physical meaning to the waves. If a single electron has a given constant velocity, the de Broglie waves have a single definite wave length and velocity, and the group extends to infinity, the "wave intensity" being everywhere the same and all positions equally probable for the electron. If the de Broglie waves form a limited group this must be the resultant of a range of wave velocities, the shorter the group the greater being the range of velocities. But we cannot imagine the electron as having more than one total velocity at an instant; the group corresponds with the range of velocities possible for the electron, that is, with the uncertainty with which theoretically the statement of its velocity must be associated. The greater the uncertainty in the velocity the shorter the group and therefore the smaller the possible range of position.

In applying this to light we have not to deal with electrons, but must postulate entities which we might call photons or quanta, possessing energy and momentum; in vacuo their velocity is the velocity of light, and, corresponding with the de Broglie waves, we have what we call light waves travelling with the same velocity. The momentum of the photon, and the energy, are proportional to the frequency of the wave. In the case of a perfectly mono-chromatic beam of light the momentum is fixed with certainty, but as we are dealing here with an infinite train of waves, there is complete uncertainty in the position of the photon. If such a beam is limited in length, for example, if a beam of mono-chromatic light is admitted through an aperture opened only for a limited time, classical methods show that the beam is no longer perfectly mono-chromatic but a complexity is introduced, there being

now a range of frequencies and therefore a range of possible values of the momentum of a photon. The shorter the beam the greater this range of frequencies and momenta, but the smaller the range of position. If the photo-electric effect could be observed, with ideal conditions, for such a beam of light the range of velocities of emission of electrons would increase as the length of the beam of light was reduced.

If this principle is correct, that we may not aspire even to an asymptotic approach to complete exactness, it leads to the conclusion that we shall never be able to make a picture of the atom which we can *prove* to be correct. Before its statement we may not have had any great expectation of doing this but we did not think that it was inherently impossible.

Of course, an immediate question arises; if the electron waves are mathematical fictions describing our knowledge or lack of knowledge concerning the electron velocity, how do we account for the diffraction effects which indicate an objective reality? If a beam of electrons falls on to a crystal surface, the widths of the various reflected beams give a measure of the range of velocities of the incident beam. If only one electron is considered, its path, after reflection, lies within a range which depends upon the uncertainty with which its velocity is associated, that is, the more accurately we can measure the velocity, the smaller the possible range of paths. It appears, at first, as though the behaviour of the electron is, to some extent, contingent on our skill in measurement, but, actually, the range of paths depends not on the precision with which we are able to measure the electron velocity, but on that with which we could do so given infinite skill, that is, on conditions of experiment. What we can say is, that certain phenomena

are observed with electrons which are consistent with the idea of electron waves satisfying definite relations between wave length, wave velocity, and electron velocity. We are unable to give any other hypothesis equally consistent with observations, but this is no proof of the reality of the waves. It is always possible that an alternative theory may be advanced, discarding, not only the idea of electron waves, but, also, the earlier concepts of the electron. The picture given on any such theory we must take simply as an expedient assisting us to formulate laws of occurrence of events.

Actually, the electron waves are on all fours with light waves in the question of objective reality. If we take the idea of photons or light quanta as the basis of our picture, light waves can be regarded as the guides or controls of the energy and momentum-carrying photons; we have similar uncertainty considerations. In each case the wave can be regarded as a mathematical device, enabling us to describe the behaviour of the "particle." We have a prejudice in favour of the light wave, because, for nearly one hundred years it was only the wave phenomena which were manifest, the corpuscular aspect of light coming into evidence later. With electrons, we had first the corpuscular aspect and now, here too, we have both.

If we consider the various phenomena of interference and diffraction of light, we find that we have phenomena, which we can reconcile with the idea of a wave motion, with a periodic effect, associated with which are a certain frequency and wave length, but, actually, we deduce these results by analogy with waves of other kinds; we have no actual knowledge that there is a frequency involved, all we can say is, that this is a way of accounting for the observations. It is true that in the case of electric

waves, which we regard as being light waves of great wave length, we have definite evidence of a frequency; we can with our eyes see periodic variations in illumination accompanying the production and reception of these waves, and we might interpret this as showing the objective reality of these long waves, and, therefore, of the shorter light waves. There can be pointed out a possible difference in the nature of the producing and receiving apparatus of the two classes of waves; in the case of light waves these are single atoms or molecules, but with electric waves bodies of relatively large size, composed of enormous numbers of atoms. Further, arise questions of the evidence of our "senses," sight, hearing, touch, etc., as a criterion of objective reality, but this is ground which the physicist has succeeded, generally, in avoiding.

Conclusion and Summary.

The outstanding points in recent developments are (1) that our physical laws do not enable us to predict precisely what will happen under specified conditions, but only to determine the relative probabilities of a number of possible events, and (2) that there is a limit to the precision with which the state of a particle can be described so that we shall never prove that any picture we make of an atom and its processes is correct.

These limitations need not be discouraging; the first in no way prevents us from making our statistical laws more and more exact, that is, the laws dealing with collections of large numbers of the particles concerning which we have probability laws; on the contrary, the greater our knowledge concerning probabilities the more satisfactory the basis for the laws describing the behaviour of the larger objects, the greater our chance of improving that

working knowledge which is the foundation of all applications of physics.

As regards the second limitation: we cannot prove that a picture is correct, but it does not prevent us from using one to assist us in using and extending our knowledge. We may use a hypothetical aether, or hypothetical waves of one kind or another, and any other devices which will assist us to formulate physical laws to assist in our problems. To be told that the aether is imaginary, that there are no such things as light waves or electron waves is no more serious than to be assured that a collection of mathematical symbols has no objective meaning. The one —like the other—might be quite meaningless and yet might be a real and powerful aid to progress.

A survey of the changes of our generation can, on the one hand, induce in us a proper sense of humility at the realisation of human limitations, but, on the other, the achievements of the great thinkers and experimenters of our age must be a source of admiration and inspiration to all who seek the truth.

A NEW COLORIMETRIC METHOD FOR MEASURING THE HYDROGEN ION CONCENTRATION OF NATURAL WATERS.

By Daphne Goulston, B.Sc.

(Communicated by Professor H. G. Chapman.)

(Read before the Royal Society of New South Wales, June 3, 1931.)

This method consists of comparing the intensity of colour produced when the indicator is added to the solution of unknown pH, with a standard depth of colour in a Dubosq colorimeter (for description of colorimeter see Hawk's Practical Physiological Chemistry, page 509).

It is evident that the indicator must have only one colour; for instance, it may be yellow in the alkaline form, but colourless in the acid form, or vice versa.

The hydrogen ion concentration of the unknown solution was calculated from the formula:—

$$H = K_{1A} \ (1 - a/a)$$

or the more convenient form:—

$$pH = \log. 1/K_{1A} - \log. 4a/1\text{-}a$$

(see Clark's Determination of Hydrogen Ions, Chap. 8), where K_{1A}, the so-called apparent dissociation constant, is a function of K, the true dissociation constant, and the constants of tautometric equilibria; and a represents the degree of colour transformation.

Technique.

0.1 cc. of 0.1% aqueous solution of para nitro phenol was carefully measured into each cup of the colorimeter. To cup (A) was added 20 cc. of N/100 NaOH (any alkali to transfer all the indicator into the alkaline form), producing a fairly deep yellow colour. This formed the standard. 20 cc. of the unknown sample was added to cup (B).

Cup (A) was set at, say, mark 20 on the scale of the colorimeter and the cup (B) was raised or lowered until a good match was obtained in the optical field. If the position of cup (B) on the scale was read at the mark 40, then a = 20/40 = 0.5, i.e., half the amount of indicator was present in the acid form and half in the alkaline form.

The method was checked by comparing a buffer solution of known pH with the standard. Kolthoff's buffer solution 0.1 M KH_2PO_4 and 0.5 M borax was employed. The mean of ten readings on the scale was taken to find a. Log. $1/K_{1A}$ or p. nitro phenol at 20°C. = 7.16. The agreement between the buffer pH figures and the standard p. nitro phenol figures is shown below:—

a	pH	pH	pH buffer
3.8/40	6.18	6.2	6.2
8.8/40	6.61	6.6	6.6
8.6/40	6.59	6.6	6.6

A 0.3% solution of meta-nitro phenol, which has a log. K_{1A} = 8.32 at 20°C. was also used as the indicator.

a	pH	pH	pH buffer
8.6/40	7.789	7.8	7.8

All experiments were carried out in a room temperature of about 20°C.

The above method was employed to find the pH of sea water. The following results were obtained:—

	Date	Indicator	pH	pH Gillespie's method
Circular Quay ..	27 Sept.	M.N.P.	7.95	7.95
Circular Quay ..	3 Oct.	M.N.P.	7.93	7.95
Circular Quay ..	4 Oct.	M.N.P.	7.93	7.95
Bottle only half full, analysed 3 weeks later ..		M.N.P. P.N.P.	7.72 7.68	7.75 7.70
Farm Cove	26 Oct.	M.N.P.	8.05	8.05
Farm Cove		M.N.P.	7.93	7.95
Coogee		M.N.P.	7.94	7.95
Bondi		M.N.P.	7.93	7.95

When this method is employed to determine the pH of a solution, three errors have to be taken into consideration, namely:—

(a) The two-acid error
(b) The salt error
(c) The temperature error

(See Michaeli Hydrogen Ion Concentration, p. 48.)

(a) In the determination of the pH by indicator methods we add to the given solution some indicator which is an acid. If the solution, e.g., sea water, is poor in buffer value, the addition of acid will alter the pH of our solution, as is illustrated in Michaelis table:—

Concentration Indicator Mols./litre	pH	Error in pH due to Indicator
0.003	7.23	— 0.29
0.0015	7.33	— 0.20
0.00075	7.41	— 0.11
0.00037	7.46	— 0.06
0.00018	7.49	— 0.03
0	7.52	|

Therefore, if 1 cc. of indicator is added to 20 cc. of the water, a correction of plus 0.2 must be made in the pH observed.

(b) Kolthoff gave a salt correction, for para nitro phenol, of minus 0.05 pH for an 0.50 N NaCl solution (see Clark, p. 121).

(c) Michaeli (see Clark, p. 131) showed the effect of temperature on the indicator employed in the following table:—

$$\text{Log. } 1/K_{1A} = \text{pH value}$$

	Temperature		
	10°C.	20°C.	30°C.
p-nitro phenol	7.27	7.16	7.04
m-nitro phenol	8.43	8.32	8.21

THE SPLENECTOMY OF TADPOLES.

By Daphne Goulston, B.Sc.
(Communicated by Professor H. G. Chapman).

(Read before the Royal Society of New South Wales, June 3, 1931.)

It is well-known that the spleen is not essential to the life and good health of adult men and women. The object of the present work was to ascertain whether the absence of the spleen influenced the metamorphosis of the larval frog in any obvious way.

The animals used in the experiment belonged to the genus *Limnodynastes* and were the largest obtainable at that period (from ponds at Marrickville, Sydney), being about 7.5 cm. in length and possessing small hind limbs. Urethane was employed as the anaesthetising agent. The animal was placed in a glass receptacle, containing about a cupful of water and a teaspoonful of urethane, until the animal just ceased to move when disturbed. This solution may be used repeatedly. The larva was immediately transferred to a wide but shallow glass dish containing tap water and some cotton wool to keep the animal in whatever position desired.

The quiescent state of the larva was maintained by the addition of several crystals of urethane whenever the animal showed signs of moving, when the skin was pinched gently with the forceps. If aquatic respiration shows signs of waning the solution must be diluted immediately for the animal is easily killed by an overdose of urethane. The tadpole was laid on the cotton wool with its left side uppermost, and a very small opening, less than 1 cm. in length,

was made through the skin and abdominal wall into the coelome or abdominal cavity. The incision was made just below where the fore limb would later make its appearance through the spiracular opening of the opercular cavity. The viscera was gently explored until the fat body, a yellow body with many finger-like protrusions, and glistening with fat globules, was found. By pulling this fat body gently and carefully, the spleen, a red organ, about the size of a pin's head or less, and rounded or angular in shape, and attached to the folds of the mesentry, was brought into view. Since it was impossible for one person to hold and ligature the spleen, this organ was simply snipped off with a scissors. The fat body broke so easily under the pressure of the forceps when searching for the spleen, that it was thought best to extirpate the entire organ in every case, to make the results comparable. In cases where the spleen could not be found immediately, the laparotomised larvae were used as controls. The wound was closed by sewing the whole integument together, using the finest "eye" catgut. Except that the catgut was stored in alcohol and the needles placed in a dilute solution of lysol, when not in use, no antiseptic precautions were practised. The needle (a straight cutting needle, one inch long) and catgut were washed in clear tap water before using them.

About one dozen of both the splenectomised and control tadpoles died within 1-2 days of the operation. Six splenectomised and ten normal larvae, during 3-4 weeks developed quite normally, as far as the eye could discern. In the case of the splenectomised tadpoles the tail diminished to a mere stump, while both forearms developed and the frog-like appearance was assumed.

The animals died, owing, I assumed, to bad aeration in the hastily improvised aquarium. The control animals,

which had been kept in an old, well-established aquarium, lived for months.

Sections, stained with haematoxylin and eosin, of the organ removed were identified histologically as splenic tissue. That the spleen had been extirpated and that no regeneration had taken place during 3-4 weeks was proved by a post-mortem dissection of the developed animal.

In conclusion, it may be stated that there was no evidence of any deviation from the normal course of metamorphosis of the tadpole following splenectomy.

VARIATIONS OF THE HYDROGEN ION CONCENTRATION OF SEA WATER.

By Daphne Goulston, B.Sc.

(Communicated by Professor H. G. Chapman).

(Read before the Royal Society of New South Wales, June 3, 1931.)

Gillespie's simple colorimetric method for obtaining the pH of solutions seemed most suitable for the purpose in hand. To prepare the standard series of colours 1 decigramme (0.1 gm.) of the dry powder of phenol red was placed in a sterile glass bottle and 5.7 cc. of N/20 NaOH were added. When the powder was dissolved the solution so formed was diluted with distilled water to 25cc. This gave a 0.4% solution of the original dye. For use in experimental work, 5 cc. of the stock solution was made up to 100 cc. with distilled water giving a 0.02% solution.

Clean rimless test tubes of uniform bore were carefully selected with the aid of a wooden peg, and also tested by pouring 10 cc. of water into each tube and discarding the unsuitable tubes. The test tubes were then washed with distilled water and steam sterilised for three hours.

The N/100 solutions of sulphuric acid and sodium hydroxide to be used were sterilised by boiling. The corks to fit the test tubes were also boiled and the wax for sealing purposes was filtered to be freed from dust. The test tubes were placed in a paired series and 0.02% phenol red solution added in the drop-ratio of :—

A series: 0.50 cc. 0.55 cc. 0.60 cc. 0.65 cc.

B series: 0.50 cc. 0.45 cc. 0.40 cc. 0.35 cc. etc.

To each test tube of one series were added 10 cc. of N/100 acid and to the other series N/100 base. One drop of pure xylene, from a capillary tube, was added to each tube to prevent growths of moulds or bacteria. The tubes were then sealed with corks that were freshly sterilised and waxed, and labelled.

A trial series of drop-ratio:—

A series: 0.555 cc. 0.550 cc. 0.545 cc.

B series: 0.445 cc. 0.450 cc. 0.455 cc.

of the indicator was made up, but since it was difficult to appreciate the difference in adjacent shades of colour in the centre of the series, the former series was employed. The pH of each pair of tubes was calculated, using Clark's dissociation constant for phenol red (phenol sulphon phthalein). Ka = 1.2 x 10 or pKa = 7.9, and employing the formula:—

Ch = Ka (undissociated molecule)/anion.

There was a difference of 0.2 pH between the figures thus obtained and those of Gillespie's drop-ratio figures, so, using I. M. Kolthoff's buffer mixture of borax and acid potassium phosphate a new colour series was obtained as follows:—

Acid phosphate of potassium was recrystallised two or three times, dried to constant weight at 110-105°C. The salt dissolved clear. High grade commercial borax was also recrystallised and constancy of weight established in a desiccator. Stock solution of 0.1 M potassium H phosphate, i.e., 13.61 gm/litre, and 0.05 M borax, i.e., 19.10 gm/litre, were made with distilled water.

The buffer series was prepared from Kolthoff's table.

Potassium H Phosphate	Borax	pH
6.23 cc.	3.77 cc.	7.0
5.81 „	4.19 „	7.2
5.50 „	4.50 „	7.4
5.17 „	4.83 „	7.6
4.92 „	5.08 „	7.8
4.65 „	5.35 „	8.0
4.30 „	5.70 „	8.2
3.87 „	6.13 „	8.4
3.40 „	6.60 „	8.6

When the drop-ratio series was compared in a comparator with the series of buffer mixtures, Clark's and Kolthoff's, were found to coincide approximately.

For collection of a sample of water, a light blue coloured bottle of common glass was cleaned and rinsed with the sea water to be tested, and a sample taken. The pH of the water was obtained by pipetting 10 cc. of the sample into a tube of the same bore as the standard pH series, and adding to this 1 cc. of 0.02% phenol red solution. The tube was then placed in the centre compartment of a comparator with a test tube of distilled water immediately behind it, and the colour compared with the shades in the prepared standard series. Two trial samples were taken from Coogee beach, and the Spit. The pH of both was 8.5 and six days later this pH was unaltered, so it was concluded that no alkali had been absorbed from the glass of the collecting bottle in any appreciable quantity. This particular kind of bottle was, therefore, considered suitable for the collection of samples of sea water. The room temperature in which the pH experiments were carried out varied from about 20° to 22°C., and the pH figures obtained were not corrected for temperature or salinity. McClendon found that under normal conditions the pH of the sea water falls 0.01 for 1°C. decline in temperature, and a correction of -0.01 should be applied to the pH for every unit rise in the salinity above 0.33%.

Of the samples taken from the coast near Sydney, Cronulla, La Perouse, Bondi, Manly, Collaroy, etc., 60% showed a pH of 8.5, and 40% gave a pH of 8.4. Since this figure is so near the end of the phenol red curve, it was thought advisable to check the figure by employing another indicator.

A stock solution of cresol red, ortho-cresol sulphon phthalein was prepared by dissolving 0.1 gm. of the dry powder in 5.3 cc. of N/20 sodium hydroxide and diluting to 25 cc. with distilled water. This 0.4% solution was 0.02% for experimental purposes. Clark's dissociation constant for cresol red is 8.3 pKa. A standard drop-ratio series with cresol red as the indicator was prepared as before. Two samples of sea water from Cremorne and Circular Quay gave a pH of 8.4 with both the phenol red and the cresol red series. The alkalinity of the sea water in contrast to the neutrality or acidic character of tap and distilled waters was also shown by means of phenolthalein and litmus paper; sea water changing sensitive litmus paper first mauve, then blue, within five minutes; both tap and distilled waters, on the other hand, turned blue litmus paper pink, the intensity of pinkness being greater in the case of distilled water than the tap. When a drop of phenolthalein was added to sea water a very distinct pink colour resulted, while tap and distilled waters, when similarly treated, remained colourless.

The hydrogen ion concentration of the sea water on the open sea shore seems to change slightly, since of the samples taken from Coogee beach, most were of a pH of 8.5, while some showed a pH of 8.4, and the pH of one sample was 8.6. As one travelled from the ocean, through the harbour and up the rivers, the alkalinity of the water decreased perceptibly within a mile or so, as is demonstrated from the following figures:—

Lane Cove River	Valentine	pH 8.4
	Tambourine	8.3
	Figtree	7.8
	Fairy Bower	7.4
Parramatta River	Harbour	8.4
	Long Nose Pt. ..	8.3
	Drummoyne	8.2
	Gladesville	8.1

This reduction of the alkalinity of the water is probably due to several factors, such as a lessening in the amount of Ca and Mg hydroxides, which cause the general alkalinity of sea water; a pouring out of fresh and brackish water from the rivers; and a proportional increase in organic life.

A modification of a Van Slyke apparatus was employed in an attempt to find the carbon dioxide content of sea water, but without success. For a pH 8.5 and 7.0 the CO_2 content was approximately 14%-15%, i.e., 14-15 cc. of CO_2 was contained in 100 cc. of sea water. The difference in the CO_2 content of water of a pH of 8.5 and 7.0 could not be measured by this method. The relation of the hydrogen ion concentration of sea water to its CO_2 tension was found in the following manner. A glass bottle of a capacity of about 560 cc. volume was cleaned, and rinsed with the sea water to be examined. About 15 cc. of sea water sample were then run into the bottle, and a minute quantity of CO_2, from a Kipp's apparatus, was run into the bottle (the CO_2 being first passed through distilled water to remove any trace of HCL vapour). The bottle was then made air tight with a vaselined glass stopper, and shaken vigorously for a few minutes. About half an hour was allowed for equilibrium to become established between the air and water. The bottle was again shaken, and a sample of the air was taken into a glass syringe, and the pH of the water was obtained immediately in the usual way. The sample of air was analysed for CO_2 in a Haldane's gas analysis apparatus. The barometric pressure, and the temperature

of the gas analysed, were also noted. A graph was obtained from separate samples of water of the same natural pH of 8.4.

This graph shows that sea water is slightly buffered, although as small an increase as 8 mm. in the CO_2 tension sufficed to alter the pH from 8.5 to 7.0. The buffer action was also shown by titration. One cc. of phenol red was pipetted into a clean test tube of the specific diameter for the phenol red series, and 10 cc. of the sample of sea water added. This was titrated with N/200 sulphuric acid until the colour was of the same tint as the pair of tubes of pH of 7.0. The colours were compared in a colorimeter. Ten cc. of the sample of sea water required 1.3 cc. of N/200 acid to increase the acidity from pH 8.5 to pH 7.0.

i.e.: 6.5×10^{-4} g.m. H ions were added to bring the pH of 1,000 cc. of sea water from 8.5 to neutrality.

9.7×10^{-8} g.m. H ions would suffice to do this in the case of distilled water.

The fact that the pH of the ocean water does not remain constant is shown in the following figures:—

Palitzsch	Black Sea	pH 8.34 (surface) 7.45 (deep)
Mayor	Yarmouth Sargasso Sea Florida	7.95 (cold) 8.25 (tropical) 8.60 (at reef flat) 8.25 (away from reef flat)
Mayor	Gulf of St. Laurence Gulf Stream	pH 8.0-8.1 8.2-8.4
Goulston	Sydney	ph 8.4-8.5 (sea shore) 8.1-8.4 (river to harbour)
Henderson and Cohn	Salinity: 30.73 34.60 0°C. 40°C.	8.03 (CO_2 tension constant) 7.87 (salinity constant) 8.35 8.32 7.95

McClendon states that it is almost certain that the CO_2 tension is the chief factor in determining the pH of oceans. When McClendon diluted sea water of pH 8.1 with an equal volume of conductivity water of pH 6, the resulting pH (using H electrode) was 8.09; while a jelly fish, pulsating in a closed vessel, changed the pH from 8.2 to 8.0 in a short time, indicating an increase of about 6.5 cc. of CO_2 per litre. He also maintains that temperature is the most important factor determining the pH of the surface water of the sea; for as the temperature rises carbon dioxide is driven out of the water and alkalinity increases; whereas if the temperature falls, the water attains an increased capacity for absorbing CO_2, derived from the animals and plants, and the Ch increases.

Sir William Herdman found that a periodic seasonal change in the alkalinity of sea water corresponded roughly with the phytoplankton annual curve.

"In early spring the rapidly developing myriads of diatoms in their metabolic processes use up the store of CO_2 accumulated during the winter, or derived from the bicarbonates of Ca and Mg, and so increase the alkalinity of the water, until the maximum of alkalinity, due to the fixation of the carbon, and the reduction in the amount of CO_2 present, corresponds with the crest of the phytoplankton curve in April or May.

The ability of different species of marine fishes to extract oxygen from sea water at different pH's varied. For example, Powers found that the Cunner was able to extract O_2 from the water when the pH was 8.4 or 6.6; whereas the optimum O_2 intake of the Mackerel was limited between pH 7.7 and 8.2. This fact may be correlated with the range of habitat of the species.

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ON THE METABOLISM OF COLD-BLOODED ANIMALS.

By Daphne Goulston, B.Sc.
(Communicated by Professor H. G. Chapman.)

(Read before the Royal Society of New South Wales, June 3, 1931.)

Introduction.

Few determinations are available concerning the consumption of oxygen and elimination of carbon dioxide by cold-blooded animals. Such determinations as have been made have not been correlated with the surface area of the animals. I have, therefore, made some determinations of the metabolism of frogs and have related the metabolism to the results of these determinations.

Method of Determining Surface Area of Frogs.

The frogs were killed by pithing the brain and spinal cord. Since the weight of a frog varies appreciably according to whether it occupies a moist or dry habitat, all the frogs were rinsed in tap water and the superfluous water absorbed by slightly damp filter paper previous to weighing. Six frogs were chosen varying in weights from 6.8 to 31.1 gm. and plaster of paris casts were made as follows:—

The frog was laid on its dorsal surface on a plate of glass with its fore and hind limbs placed so as to be freed from touching the trunk of the animal. No attempt was made to separate the digits of the manus and pes.

The animal was effectively halved by outlining the body, fairly thickly, with plasticene, so that the plasticene made contact with the skin of the animal at approximately

half the thickness from the dorsal to ventral surface. A plasticene wall about $1\frac{1}{2}$ ins. high was then built around this structure, and a thin layer of oil was painted over the plasticene. Fresh plaster of paris was added to water and a fairly heavy creamy consistency was obtained, and the mixture immediately poured into the frog-plasticene structure.

When the plaster had hardened (about 20 minutes later), all the plasticene was removed, and the plaster surrounding the frog was painted with shellac, which dried almost immediately, and then with oil. A fresh plasticene wall was now built round the half plaster cast and plaster of paris was poured into the plasticene cast structure and again left to harden.

The two halves were gently pulled apart and the dead frog carefully removed. The casts were shellaced and left to dry.

The casts were next lined, as thoroughly as possible, with wet japanese silk by means of a hard brush and commercial adhesive paste. When dry the lining was gently pulled free from the cast and the "frog shape" cut into fragments small enough to lie flat.

A sunlight print was obtained of all the fragments, and the weight and area of the sensitised paper obtained. Each small piece representing a portion of the surface area of the frog was next carefully cut out, and the weight of the sum of these pieces obtained.

If Y sq. cm. equal the total area of the sensitised paper
Z gm. equal the weight of the sensitised paper
X gm. — weight of fragments

$$\text{Surface area} = \frac{Y.X}{Z}$$

The accuracy of the method was tested by pasting japanese silk around a billiard ball, and treating this surface covering in the same way as above.

Calculated Surface Area.	Experimental Surface Area.
80.20 sq. cm.	80.65 sq. cm.
	80.00
	81.50
	80.30 sq. cm.

The surface area figures for the frogs were less accurate, due to the difficulty of lining the cast. For example :—

Weight—frog 31.1 gm.	Surface Area.
	100 sq. cm.
	102
	105
	101
Mean	102 sq. cm.

Using Meeh's formula relating the surface to the volume:

$$\text{Surface} = \text{K Volume}^{2/3}$$

The specific gravity is practically constant, so that weight may be substituted for volume in this expression :—

$$\text{S.A.} = \text{K}^3\ \text{W}^2$$

Figures obtained for K constant as follows :—

K	10.26	
	11.63	
	12.06	
	11.58	
	11.79	
	12.30	
	11.60	Mean.

Inabas (Archiv. Anat. Physiol. 1911) found:—

K for lizards = 12.4 (wt. 4 to 8 gm.)
12.79 (wt. 20 to 26 gm.)

K for frogs = 4.6

To obtain this constant K, Inabas measured the skin after its removal from the animal.

This method would only give a true figure when the skin neither stretches nor shrinks on its removal from the body. Inabas' constant for lizards is of the right order of magnitude, but his frog constant is a long way out, due to the shrinkage of the frog's skin.

The following figures for K have been found for various animals:—

K Dog = 10.10 (Wt. 1 kg. approx.)
Cat = 10.27 (Wt. 1 kg. approx.)

(Karl Thomas, Archiv. Anat. Physiol. 1911)

K Man = 12.5
Dog = 11.2—10.3
Cat = 9.9
Mouse = 11.4

(Rogers—Comparative Physiology, 1927.)

My surface area figures were obtained from experiments with winter frogs, so that probably a different value for constant K would be found for female frogs, during the breeding season, due to their increase in girth.

Cowgill and Drabkin (Amer. Journ. Physiol. 1927, No. 1) experimented with dogs and have added to the Meeh Rubner surface area formula to allow for the nutritive state of the animal, producing the following expression:—

$$S \text{ sq. cm.} = KW^{0.7} \text{ gm.} \times N_m / N_{obs}$$

where N_m/N_{obs} = nutritive state correction

N_{obs} = $W^{1/3}$/length of individual in question

N_m = Maximum possible $W^{1/3}/L$ for the species.

Dreyer found, and Cowgill and Drabkin confirmed, with the data from Stewart and Thomas, the fact that the exponent of the weight should be 0.71 instead of 0.667 (2/3 power).

With exponent	0.667	K mean is	± 5.4%
,, ,,	0.71	,,	± 2.9%

Frog	Weight	Length	N_{obs}
A	31	6.8	0.462
B	13	5.1	0.461
C	7	4.5	0.425
D	9	5.1	0.407
	10	5.1	0.423
E	16	5.9	0.427
F	19	6.1	0.437
F_1	23	6.1	0.466

F_1 is frog F allowed to remain between wet filter paper overnight.

The Metabolism of Frogs.

The only data concerning the direct calorimetry of frogs was obtained by A. V. Hill (Journ. of Physiol. Vol. 13, 1911). Hill designed a micro-calorimeter. Two thermos flasks were arranged each in contact with one junction of a sensitive galvanometer, which was connected to a copper constant thermocouple: so that when the animals plus some water were placed in one flask, and some water in the other flask, the deflection of the galvanometer mirror gave the difference of temperature between the two flasks. The difference was increased by the heat-producing activity of the living animals.

100 cc. frogs (8 frogs)
150 cc. water
in A flask.
285 cc. water
in B flask.

Hill found that the living resting frog produced about 0.45 calories/cc. frog at a temperature of 19° C.

The average volume of a frog was 12.5 cc. and the surface area was 62 sq. cm. (using D. Goulston's constant K = 11.6).

A resting frog, therefore, produced 20.77 cals./sq. metre /day.

Hyla Aurea.

The following experiment was an attempt to ascertain directly the resting metabolism of an individual frog. The same frog was used throughout all experiments.

Only water had been supplied to the animal one week (at least) previous to, and during, the experiments.

The frog was placed in a wide-mouthed jar of capacity of 1150 cc. The jar was closed with a stout rubber stopper through which passed an "inlet" and "outlet" glass tubing. The inlet tube was connected by rubber tubing to a series of five absorption tubes containing 40% KOH; while the outlet tube was connected to an aspirator. A cloth was draped round the jar to prevent the animal from being disturbed.

Air freed from CO_2 was drawn through the experimental jar for one hour. The outlet tube was then disconnected from the aspirator and some air drawn through into a sampling tube. The inlet and outlet tubes were immediately closed with pinch-cock stoppers. (Later glass taps were substituted.)

The animal was allowed to remain thus for a period of three hours. The tap water, which operated the aspirator, was allowed to continue to run so that the animal would not be disturbed by an unnecessary change in its vicinity.

After the experimental period had elapsed, another sample of air was taken from the jar, care being taken to obtain a well-mixed sample by raising and lowering the plunger of the sampling tube several times.

The "before" and "after" samples of air were analysed in a Haldane gas analysis apparatus. The following figures were obtained:—

PRELIMINARY METABOLISM FIGURES FOR RESTING FROGS.

Date	CO_2 % expired	O_2 % absorbed	Time hours	Weight gm.	Calories/sq. metre/day	R.Q.	Temperature 0° C.
4	0.46	0.51	3	16.1	27.88	0.90	23
8	0.34	0.38	3	14.6	22.46	0.97	24
9	0.29	0.35	3	14.0	20.24	0.83	24
10	0.22	0.30	3	14.6	17.45	0.73	21
11	0.22	0.30	3	14.2	17.03	0.73	19.8
12	0.19	0.27	3	14.4	15.78	0.72	20.3
17	0.17	0.23	3	14.1	13.48	0.74	19
19	1.39	1.65	22	13.4	14.11	0.84	20-22

Weight	Surface Area
13 gm.	64.2 sq. cm.
14 gm.	67.4 sq. cm.
15 gm.	70.5 sq. cm.
16 gm.	73.7 sq. cm.

The above figures show that the metabolic rate of a resting frog falls during starvation.

Hill found, as shown in his graph, that the heat production of frogs, kept without food, fell from an initial high value of 0.5 calories per cc. frog to 0.3 calories at

20° C. This fall took place gradually, and was not complete until about 15 days.

This corresponds to a fall of metabolism from 24 calories/sq.m./day to 14 calories/sq.m./day.

The rate of heat production of a frog is increased 2-3 times by a rise of 10° C. as demonstrated below:—

27° C.	..	0.7 calories/cc./frog/hour
20° C.	..	0.5 „ „ „ „
0.3° C.	..	0.2 „ „ „ „

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THE MINERALOGY AND ORIGIN OF THE NATURAL BEACH SAND CONCENTRATES OF NEW SOUTH WALES.*

By H. F. Whitworth, B.Sc.

(With twenty Text Figures.)

(Communicated by C. A. Sussmilch.)

(Read before the Royal Society of New South Wales, June 3, 1931.)

Occurrence.

At many places along the coast of New South Wales, between the mouth of the Shoalhaven River on the south, and the Queensland Border on the north, deposits of naturally concentrated heavy minerals occur on the beaches. The minerals have been concentrated by wave action during heavy south-east gales, and the deposits are usually best developed from the centres to the northern ends of the beaches. The most extensive deposits occur on the beaches to the north of Port Macquarie, those on the Southern beaches being much smaller. Raised beaches, only a few feet above sea-level, occur on the North Coast, and many of these contain layers of heavy mineral concentrates. In localities such as these, in which the waves are eroding the raised beaches, the deposits of concentrates on the present day beaches are particularly heavy, sometimes reaching a thickness of three feet, a width of twenty yards, and a length of over a mile after a heavy storm.

During periods of fine weather, the concentrates dry and become remixed with the beach sand, largely by the action of the wind, but at each high tide, a line of black sand is usually left at high water mark, thus indicating the presence of heavy minerals in the sand.

* Published by permission of the Under-Secretary for Mines.

Economic Importance.

The beaches and raised beaches of the North Coast have been worked intermittently during the past thirty-five years or so, for their gold, platinum, tin and monazite contents, but have failed to yield a satisfactory return. A large part of the work has been done by fossickers, who confined their attention to the heavy concentrates or "sniggers" formed during storms. More recently some attention has been paid to some of the South Coast beaches, and in 1925 a little cassiterite and gold were obtained from the beach at Thirroul. As the amount of concentrate on this beach is small, operations were conducted on a small scale, and have since been abandoned. Although both gold and cassiterite are known to occur on other beaches on the South Coast, little or no work has been done on them.

Attention is now being paid to some of the North Coast beaches as a possible source of zircon and rutile, the former for use in the manufacture of zirconia, which is now used as an opacifier in the enamelling of iron and steel, and the latter for the manufacture of titanium white, a pigment of great covering power, now finding an extensive use in the paint industry.

Composition.

The colour of the natural concentrates varies from a pale grey to a very dark grey, according to the amount of ilmenite present, and in some localities, it is so dark in colour that it is commonly known as "black sand." Owing to the fineness of the mineral grains, and their high degree of rounding, the concentrate is extremely mobile when dry.

A microscopic examination reveals the fact that the grading is very even and that the main constituents are zircon, ilmenite and rutile. As these three minerals have similar specific gravities, and as the grains are of approxi-

mately the same size, the percentage weight of each in a given sample may be determined with a fair degree of accuracy by a simple count of the number of grains of each mineral present in a small sample. This count is conveniently made with the aid of a microscope with a magnification of about 200 diameters, immersing the sample in a highly refracting liquid. Nitro-benzene was found to be suitable for this purpose, for, its refractive index being about 1.55, any quartz grains present are rendered almost invisible in ordinary light, whilst zircon and rutile grains stand out in high relief owing to their much higher refractive power. Providing that more than 1000 grains are counted in at least ten different fields of the microscope, the error in estimating the percentage weights of the minerals present does not appear to be high.

The approximate mineralogical composition of a number of samples of natural concentrates from different localities is given below.

Locality.	Zircon.	Ilmenite.	Rutile.	Other Minerals.
Corrumbin ..	53%	27%	13%	7%
Byron Bay ..	43%	36%	13%	8%
Ballina	62%	26%	7%	5%
Berrie Point ..	75%	14%	9%	2%
Fingal Beach..	54%	30%	11%	5%
Iluka	52%	28%	18%	2%
Collaroy	40%	43%	15%	2%
Thirroul	60%	25%	13%	2%
Terrigal	45%	39%	13%	3%

The term "Other Minerals" in the above table does not include quartz, the presence of which implies imperfect concentration. Some of the samples examined contained about 25% of quartz whilst others were practically free from this mineral. Quartz is easily removed from the heavy minerals by panning or by shaking and dry blowing. Either of these methods will yield a concentrate practically

free from quartz, with the loss of very little of the heavy minerals present.

The following analyses, published in "The Mineral Industy of New South Wales" (N.S.W. Geological Survey 1928) serve to illustrate the chemical composition of the sands:

	No. 1	No. 2
SiO_2	27.46	20.36
ZrO_2	50.78	43.77
TiO_2	14.00	23.50
Al_2O_3	1.72	0.34
Cr_2O_3	0.42	0.34
FeO	4.83	4.48
MnO	0.25	trace
CaO	trace	absent
MgO	0.42	0.44
P_2O_5	0.24	1.25
Rare Earths	trace	1.61
Organic Matter	trace	0.32
SnO_2	trace	3.81
Gold	1 dwt. 7 gr. per ton	1 dwt. 10 gr. per ton
Platinoid Metals	less than 10 gr. „	less than 10 gr. „

No. 1.—Natural beach sand concentrate from between the Richmond River and Evans Heads. Analyst, J. C. H. Mingaye.

No. 2.—Natural beach sand concentrate from two miles south of Evans Heads. Analyst, H. P. White.

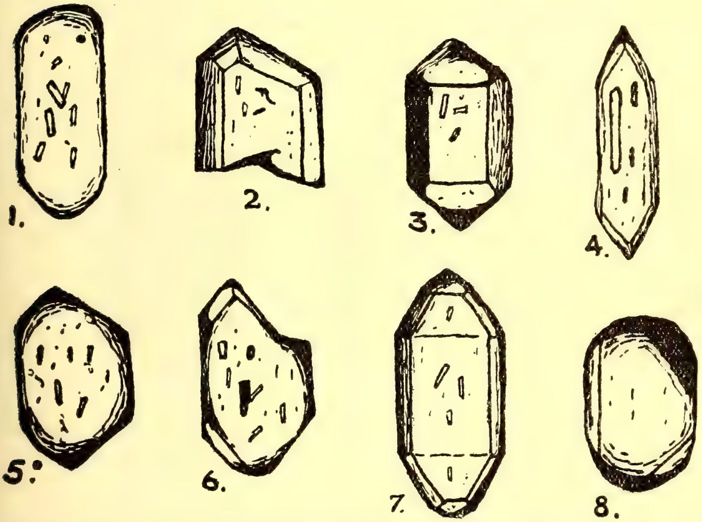
The writer has examined many samples of these naturally concentrated sands under the microscope, and in addition to zircon, ilmenite and rutile, the following minerals have been recognised:—

Leucoxene	Green spinel
Epidote	Brown spinel
Chromite	Cassiterite
Magnetite	Chalcedony
Limonite	Sapphire
Tourmaline	Pyroxenes
Monazite	Hornblende
Xenotime	Andalusite
Garnet	Staurolite
Pleonaste	

Raggatt (Bulletin No. 13 Geological Survey of New South Wales) states that Columbite is present in some cases. Owing to the opaque nature of this mineral, and the presence of a large amount of ilmenite, which is also opaque, it is impossible without the aid of magnetic separation and chemical tests on the separated fractions, to verify the presence of Columbite.

Description of the Minerals Present.

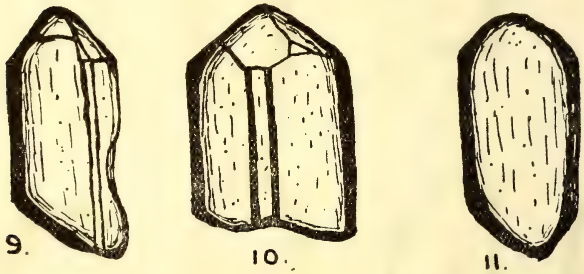
The *zircon* is nearly all of the colourless variety, although a few pale pink and pale blue grains are present. It occurs both as well rounded grains and as perfect doubly-



Figs. 1-8. Zircon crystals separated from beach sand concentrates. Approximate length 0.2mm.

terminated, pyramid capped tetragonal prisms. The crystals average about .2 mm. in length and about .1 mm. in breadth, whilst the rounded grains average about .15 mm. in diameter. The occurrence together of well rounded grains and perfectly preserved crystals, seems to imply that the

crystals have been transported from their original source as inclusions in some other mineral which has protected them from erosion, and which has liberated them comparitively recently. The zircon is easily recognisable from its high refractive index, brilliant lustre on crystal faces, and its high double refraction. The double refraction is so high that most grains show only a high order white interference colour, though some show pale pinks and greens on the edges. Inclusions are common, some are definite crystals of rutile, whilst others appear to be hollow cavities, irregular in some cases, and elongated parallel to the "C" axis of the zircon, in others. Tiny dust-like inclusions, probably of oxide of iron, occur along definite zones in many crystals.



Figs. 9-11. Rutile crystals separated from beach sand concentrates. Approximate length 0.2mm.

Rutile occurs as broken or imperfect crystals, or as rounded grains. The colour varies from a deep reddish brown through various shades of brown to a deep yellow. Many of the deeper coloured grains are almost opaque, and unless examined carefully in a very strong light, may be mistaken for ilmenite. The lustre on crystal faces and on freshly broken surfaces is very high, and the refractive index is so high that the lustre is quite noticable even when

immersed in nitro-benzene, the refractive index of which is about 1.55. The double refraction of rutile is high, and interference colours are masked by the strong natural colour. Pleochroism is weak, and is only noticeable in the lighter coloured varieties. In size, the rutile grains are approximately equal to the zircons, the crystals averaging about .2 mm. in length, and the rounded grains about .15 mm. in diameter.

Ilmenite occurs both as imperfect crystals and as rounded grains. It is quite opaque, and of a bluish black colour by reflected light, whilst the lustre is somewhat metallic. Many of the rounded grains of ilmenite show curiously shaped cavities in their surfaces. These grains are probably the eroded remains of the skeletal crystals which are so characteristic of ilmenite. Whilst the average grain size of the zircon and ilmenite is approximately the same, many of the ilmenite grains are very small, some being less than 0.05 mm. in diameter.

Leucoxene occurs as a brown, yellow or white coating on the ilmenite grains. Some of the grains of ilmenite are only partially covered with leucoxene, whilst others appear to have been entirely replaced by that mineral.

Epidote occurs rather sparingly as rounded yellowish green grains, generally slightly clouded through alteration. It is recognisable by its high refractive index, weak though distinct pleochroism, bright interference colours, and the clouding previously mentioned. The amount of epidote varies greatly in different samples of sands. As the specific gravity of epidote (3.4) is considerably below that of zircon, ilmenite and rutile (4.53, 4.65, and 4.25 respectively) its presence is an indication of imperfect concentration.

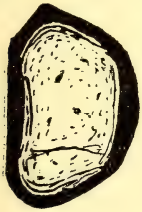
Chromite. The presence of small amounts of chromic oxide is shown by the analyses previously quoted, and a careful search reveals the presence of chromite in dark brown flakes which are almost opaque, being translucent on the thin edges only. The flakes are isotropic, and possess a very high refractive index. A few brown opaque octohedral crystals of chromite have been noted in some cases.

Magnetite occurs rather sparingly and is most easily detected by means of a magnet. The grains separated in this manner are jet black to brownish black in colour, and are often partially altered to limonite. Some perfectly formed octohedral crystals are present.

Limonite is present as small reddish brown earthy opaque grains, some of which appear to have a concentric structure. Much of the limonite present appears to be an alteration product of magnetite.

Tourmaline is very variable in amount, being very rare in some sands and forming up to 2% of the volume of others. As in the case of the epidote, this variation may be accounted for by the comparatively low specific gravity of the tourmaline (about 3.1). The tourmaline occurs both in the form of rounded grains and as short prismatic crystals with rounded ends. The colours are very varied, blue, pink, brown, black, and yellow grains being present. The pleochroism is very strong, changes being from colourless, yellow or brown to black, blue to pink, blue to colourless, blue to brown, pink to colourless and pink to brown. The characteristic absorption, which is greatest when the prism edge of the crystal is parallel to the vertical cross hair of the microscope, serves to identify any crystals of tourmaline present. The rounded grains are quite easily recognisable by their comparatively low refractive index and low double refraction, and their strong pleochroism.

Monazite, owing to its softness, occurs mainly as rounded grains which are slightly below the average grain size of the sands. Many of the grains have a peculiar bean-like or pear-like shape which seems to be characteristic (see figs. 12-14). The colour is pale yellow or yellowish green and pleochroism is absent. The refractive index is high and the grains show a characteristically pitted surface.


12.


13.


14.

Figs. 12-14. Monazite grains separated from beach sand concentrates. Approximate length 0.15mm.

The double refraction is about the same as that of zircon, and the grains show a high order white interference colour sometimes showing pale pinks or greens on the thin edges. The amount of monazite varies in different sands, in some cases being present to the extent of over 1%. The specific gravity of the monazite is sufficiently above that of the zircon, ilmenite and rutile to allow it to be concentrated by panning.

Xenotime. In the absence of micro-chemical tests, the determination of this mineral is in doubt, but in certain analyses both the phosphorous pentoxide and rare earths are shown in excess of that required for the monazite present. This implies the presence of another phosphate mineral of the rare earth group. Many of the sands examined contain a yellow mineral, often opaque through alteration, crystallising in a manner to the zircon, and

having a very high refractive index and double refraction. This mineral has been provisionally classed as xenotime.

Garnet is present in practically all the sands examined, and occurs as irregularly shaped fragments which are not well rounded. Perfectly formed crystals are not present, although occasionally a crystal face may be seen. Both pink and colourless varieties are present. The combination of high refractive index and isotropic character serve for its identification.

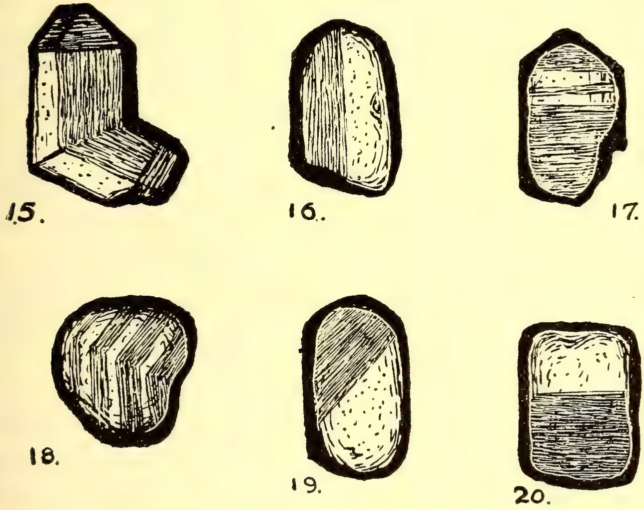
Pleonaste is a very rare constituent, and has been definitely recognised in only a few of the many samples of sand examined. It occurs as irregularly shaped grains, which are black in colour by reflected light, and either a dark green or grey on the thinnest edges by transmitted light, the colouring being so strong that the centres of the grains are opaque.

Green Spinel is slightly more abundant than the pleonaste, and occurs as bright green grains which may be recognised by their high refractive index and isotropic character.

Brown Spinel occurs rather sparingly as dark brown translucent, isotropic flakes, having a high refractive index.

Cassiterite usually is a rare constituent, but in some cases owing to its relatively high specific gravity (6.65), it has been concentrated locally and samples containing as much as 25% of this mineral have occasionally been obtained. Most samples of the sands will yield a concentrate rich in cassiterite and monazite by panning. The identification of cassiterite is somewhat difficult owing to its variable colour. The colours are grey, yellowish brown, dark brown, brownish red and colourless. Pleochroism is very faint, and is best seen in the grey coloured grains. Well preserved crystals are rare, but a few prismatic

crystals and geniculate twins have been seen. Many grains are either parti-coloured or zoned, which is a very useful character in the determination of cassiterite. The colour banding in some grains shows sharp changes of direction, as in Fig. 18. Such grains are evidently all that remains of an originally twinned crystal. The refractive index is high and the double refraction is so high that interference colours can seldom be seen even on thin edges.



15. 16. 17. 18. 19. 20.

Figs. 15-20. Cassiterite crystals separated from beach sand concentrates. Approximate length 0.15mm.-0.2mm.

Chalcedony is present both as angular fragments and as rounded grains which are either colourless or pale green. It is most easily recognisable by the fact that it fails to extinguish when rotated between crossed nicols, owing to its cryptocrystalline character. Its presence, like that of quartz, implies imperfect concentration.

Sapphire is a rare constituent, and occurs as flat basal cleavage plates. It is recognisable by its high refractive

index, weak double refraction, pale blue colour and faint pleochroism.

Pyroxenes. Two varieties of pyroxene are present, one being colourless, and the other being pale green and pleochroic, changing to a pale pink when rotated between crossed nicols. The colourless variety is often much clouded by alteration, and is possibly diopside. The coloured pleochroic variety is apparently hypersthene.

Hornblende is very rare and occurs as cleavage fragments. It is green in colour, strongly pleochroic, and can be identified by its oblique extinction, comparatively low refractive index and double refraction, and by its well developed cleavage.

Andalusite occurs very sparingly as rounded grains, slightly above the average grainsize of the sand. It is recognisable by its comparatively low double refraction and its pleochroism, the colours observed being pale pink or pale bluish green, changing to colourless when rotated between crossed nicols.

Staurolite is somewhat irregular in its distribution, and apparently is more abundant in the concentrated sands from the South Coast than in those from the North Coast. It occurs as rounded grains of a brownish red colour, and is identifiable by its strong pleochroism and bright interference colours. Many of the grains of staurolite contain small inclusions which all elongated parallel to the long axis of the staurolite. Some of these inclusions are surrounded by dark haloes in the staurolite.

In addition to the above minerals, there are at least three others which have not yet been definitely identified. One of these is dark brown in colour and has a very high refractive index and double refraction, and is generally

clouded through decomposition. This mineral is possibly sphene. Another mineral is brownish yellow in colour, quite opaque, and occurs as rounded grains with a brilliant lustre. The other unidentified mineral occurs as small prismatic crystals which are dark brown in colour, have straight extinction, and are almost opaque.

Origin.

The late J. E. Carne, in discussing the auriferous beach sand concentrates of the North Coast, suggested the following possible sources:—

(a) The Siluro-Devonian rocks.

(b) The Clarence River Coal Measure sedimentary rocks.

(c) The early river channels, i.e., drifts under the Tertiary basalts.

(d) Auriferous basalt at the Richmond River Heads.

(e) The present drainage channels from the Eastern margin of the stanniferous rocks of New England.

In the Annual Report of the Department of Mines for the year 1895, Carne discusses all of the above possibilities, and finally favours the theory that the early drainage channels are the source of the concentrates. In view of the fact that concentrates, similar to those of the North Coast, occur on the beaches between the mouths of the Hunter and Shoalhaven Rivers, in districts in which no Tertiary drifts are known, the writer began a series of experiments to determine whether the Triassic sedimentary rocks might not be their source.

Samples of Triassic sandstone from around Sydney were crushed and concentrated by panning, and some interesting results thus obtained. Six samples, each of 1000 grams, were treated by this method and yielded the following amounts of heavy mineral concentrates:—

Yellow sandstone	Dawes Point	.74 gms.
Yellow sandstone	Mosman	.86 gms.
Ferruginous sandstone	Willoughby	.45 gms.
White sandstone	Sailor's Bay	.22 gms.
White sandstone	Wynyard Square	.65 gms.
Yellow sandstone	Miller's Point	.35 gms.

A sample of Triassic sandstone from Broke, near Singleton, yielded only .11 gms. of heavy minerals per 1000 gms.

Several samples were treated in duplicate in order to determine whether the variations in the amounts of concentrate obtained were due to experimental error or not.

In each case the experimental error was found to be small, and it thus appears that there is a considerable variation in the amounts of heavy minerals present in different horizons of the Triassic Series.

A sample of Upper Coal Measure sandstone from near Muswellbrook yielded 0.5. gms. of heavy minerals per 1000 gms.

After warming the concentrates obtained from the sandstone with dilute hydrochloric acid, to remove iron stainings and to dissolve any particles of metallic iron introduced during crushing operations, it is seen that they bear a strong resemblance to the natural beach concentrates. In all cases they consist mainly of zircon, ilmenite and rutile, together with most of the other minerals found on the beaches. In addition to zircon, ilmenite and rutile, the following minerals have been observed:—

Haematite	Monazite	Cassiterite
Limonite	Staurolite	Tourmaline
Garnet	Epidote	Pyroxenes
Magnetite	Hornblende	

The relative proportions of zircon, ilmenite and rutile in the concentrate obtained from the yellow sandstone from Dawes Point are as follows:—

Zircon	36.6%
Ilmenite	31.3%
Rutile	23.0%
Other minerals	9.1%

The main differences between the concentrates obtained from the sandstones and the natural beach concentrates are the smaller degree of rounding in the former, and the higher percentage of monazite, epidote, staurolite, hornblende and pyroxenes.

The occurrence of heavy minerals in the Triassic sandstone near Sydney and the Upper Coal Measure sandstones near Muswellbrook leaves little room for doubt as to the origin of the concentrates on the beaches between Newcastle and the mouth of the Shoalhaven River. It is suggested by analogy, that the beach sand concentrates on the North Coast have been derived from the Triassic Series of the Clarence River District. The writer has not yet had an opportunity of preparing a concentrate from the Clarence River sandstones, but the preparation and examination of such a concentrate should prove whether the beach concentrates on the North Coast have been derived from this source.

The origin of the gold and platinum in the beach sand concentrates is, however, still in doubt. As the amounts of concentrates obtained from the sandstones were too small to allow of assays for gold and platinum being carried out, it is not known whether these metals are present in the Triassic sandstones. It is suggested that the gold and platinum must be regarded as local additions to the zircon-ilmenite-rutile concentrate, as they only occur at a few

localities along the coast, whilst the zircon-ilmenite-rutile concentrate has a very wide distribution.

Acknowledgments.

The writer's best thanks are due to Mr. D. H. Newland, State Geologist, of New York, for assistance in the identification of certain minerals present in the sands examined, and to Mr. M. Morrison, Curator of the Mining Museum, Sydney, for information regarding the occurrence of the deposits of heavy mineral concentrates on the beaches of the North Coast of New South Wales.

References.

References to the occurrence of the North Coast beach sand concentrates will be found in the following:—

Annual Report, Department of Mines, N.S.W., 1895. Report by J. E. Carne.

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THE CELLULOSES OF TWO WATER PLANTS, *OTTELIA OVALIFOLIA* (RICHARD) AND *EICHORNIA CRASSIPES* (SOLMS).

By John Campbell Earl, D.Sc., Ph.D., and Thelma Muriel Reynolds, M.Sc.

(*Read before the Royal Society of New South Wales, June* 3, 1931.)

Apparently celluloses from most sources are identical. One notable exception is the cellulose of *Posidonia australis*, and a preliminary examination (Arneman and Earl, this Journ., 1929, *63*, 44) indicated that another water plant (*Potamogeton sp.*) might possibly prove to differ from the usual standard in respect of its cellulose.

The present communication deals with an attempt to compare the celluloses of two water-plants, which were available in quantity, with the standard, cotton cellulose. In comparisons of this kind, a difficulty always met with is that of preparing a product which can reasonably be regarded as a pure cellulose. The two plants examined, *Ottelia ovalifolia* and *Eichornia crassipes*, proved to be no exception to the general rule. When a number of the recognised methods for isolating celluloses were applied to these plants, products were obtained which yielded triacetates whose optical rotations differed widely from the accepted standard of $[\alpha]_D = -21$ to $-22°$ of cotton cellulose triacetate. It was apparent, however, that the

employment of these methods had not led to the isolation of "pure celluloses," since certain supplementary treatments profoundly modified the properties of the products, eventually bringing them much closer to the standard.

The following four methods were adopted:—

(1) The washed leaves were boiled for half an hour with 1 per cent. sodium hydroxide solution. The dark-coloured, finely divided mass was washed well with water and then submitted to the action of chlorine gas, after which it was again washed with water and extracted with boiling alcohol. The chlorination and extraction with alcohol were repeated.

(2) (Cross and Bevan's method.) The washed leaves were boiled with 1 per cent. sodium hydroxide solution and chlorinated as in method (1). After washing, the chlorinated material was immersed in a cold 2 per cent. solution of sodium sulphite, which was then heated to boiling for two or three minutes. After filtering and washing the chlorination and extraction were repeated.

(3) After the initial alkaline treatment, the material was boiled for $1\frac{1}{2}$ hours with 2 per cent. sulphuric acid, before chlorination and extraction with sodium sulphite as in method (2).

(4) (c.f. Link, J.A.C.S. 1929, *51*, 2506). The air-dried leaves were shredded and extracted in a Soxhlet apparatus for 24 hours with 95 per cent alcohol. After removal of the solvent by a current of dry air, the material was further extracted for 26 hours, with 99 per cent. alcohol. It was again dried, and was then extracted for 26 hours with benzene. At this stage the material was ground in a corn mill and passed through a 30 mesh sieve. After washing with hot water it was allowed to remain for 29

hours, with occasional stirring, in contact with 1 per cent. ammonia solution. After washing with water a further 17 hours treatment with 1 per cent. ammonia solution was applied. The material was then chlorinated and treated with sodium sulphite as in method (2).

Methods (1) and (2) yielded products from which considerable quantities of furfural could be obtained by distillation with 12 per cent. hydrochloric acid. A supplementary extraction with 2 per cent. sulphuric acid, as applied in the case of *Posidonia* (J. Chem. Soc. 1923, *123*, 3223), caused a loss in weight of 30 to 40 per cent., which was not repeated on further extraction. In the case of *Ottelia* cellulose a prolonged treatment (10 hours) with boiling 12 per cent. sodium hydroxide solution was found also to bring about a loss in weight of over 50 per cent.

The celluloses obtained by the various means were compared as before, (Arneman and Earl, loc. cit.) by determining the optical rotations of the triacetates prepared by Barnett's method.

Since there is always the possibility that any chemical treatment applied to a cellulose may bring about a certain amount of break-down of the molecule, it was considered advisable to determine the viscosities of solutions in chloroform of each of the triacetates under examination. A marked lowering of the viscosity might be interpreted as indicating molecular degradation. It should be noted, however, that the values given indicate merely flow-times in a particular viscometer, and can in no way be regarded as absolute, reproducible results.

The results obtained are summarised in the following table, values for wheat-straw and cotton celluloses being inserted for comparison purposes:—

TABLE I.

Material.	Method of Extraction.	Cellulose Triacetate.		Triacetate from acid-treated Cellulose.		Triacetate from alkali-treated Cellulose.	
		$[\alpha]_D^{14\text{-}17°C}$	Viscosity*	$[\alpha]_D^{14\text{-}17°C}$	Viscosity*	$[\alpha]_D^{14\text{-}17°C}$	Viscosity*
Ottelia ovalifolia ..	1	-3.9	163	{ -16° / -16.75°	72	-21.5°	96
Eichornia crassipes ..	1	-6.4	164	-15°	77	—	—
" " ..	2	-10	113	-16.25°	68	—	—
" " ..	3	{ -16.25 / -18.5	94	— / —	— / —	— / —	— / —
" " ..	4	-20.4	78	—	–	—	—
Wheat Straw	2	-33.75	99	-25°	89	—	—
Cotton	—	-21.4°	136	-20.5°	65	—	—

* Time of flow in seconds of a 0.8 per cent. solution in chloroform at 20°C.

Variations in the application of the acetylation method have little effect on the optical rotation of the triacetate of cotton cellulose, but, in general, the longer the duration of the operation, the lower the viscosity of the triacetate produced. Treatment of cotton cellulose prior to acetylation with 1 per cent. sulphuric acid at 90°C for one hour lowered the viscosity of the triacetate considerably, and repetition of the treatment caused a slightly greater lowering. In this comparison, summarised in Table II, the triacetates were prepared under carefully standardised conditions.

TABLE II.

Material	Triacetate	
	$[\alpha]_D^{15°}$	Viscosity*
Untreated cotton cellulose	–21°	436
Treated once with acid	–19.7°	181
Treated twice with acid	–19.3°	153

* Time of flow in seconds of a 2 per cent. solution in chloroform at 25°C.

It is probable, therefore, that in the water-plants under examination, the celluloses are identical with cotton cellulose. The inevitable association of other materials with

the celluloses, prevented "pure celluloses" from being isolated, and the acid treatments resorted to caused some molecular degradation with a consequent lowering of both optical rotation and viscosity of the final cellulose triacetates.

Thanks are due to Science and Industry Endowment Fund for a contribution towards the expenses of this investigation.

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PHYSIOGRAPHY OF THE BATHURST DISTRICT OF NEW SOUTH WALES.

By C. A. SUSSMILCH, F.G.S.

(With Plates I and II and two Text Figures.)

(Read before the Royal Society of New South Wales, July 1, 1931.)

The region referred to in this paper occurs in the State of New South Wales immediately to the west of the Blue Mountain tableland. It includes the eastern part of the County of Bathurst, the south-western part of the County of Roxburgh and the north-western part of the County of Westmorland. Where these three counties meet there lies the city of Bathurst, approximately in the centre of the region to be described. The main western railway line traverses the centre of this region from east to west.

That part of this region which in this paper is called the Bathurst Senkungsfeld is an approximately rectangular area with its longer axis about 22 miles in length, lying in a north north-western direction; its east-west axis is about 19 miles in length. This region has a general elevation of about 2400′ and is surrounded on all sides by higher tablelands; its approximate extent is shown on the map—Fig. 1. To the north, west and south-west lies the Orange tableland with a general elevation of about 3100′. To the east lies the Mt. Lambie tableland (the western portion of the Blue Mountain tableland) with a general elevation of about 4100′, while to the south-east lies the Oberon tableland with an elevation of about 3600′. The junction between the Bathurst Senkungsfeld and the surrounding tablelands is always a well-marked scarp, the

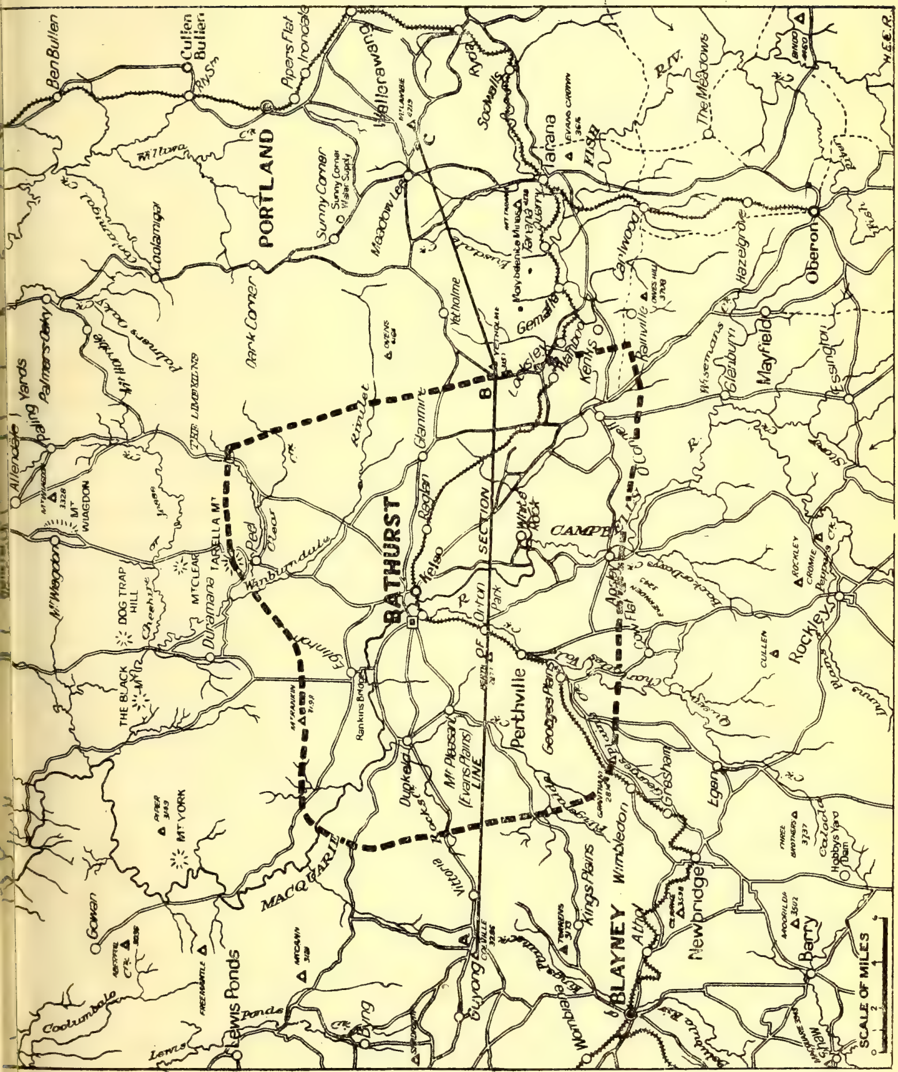

Fig. 1. *Area of the Bathurst Senkungsfeld shown by broken line*

change in elevation between it and its surroundings being everywhere an exceedingly abrupt one. The surface of the Bathurst Senkungsfeld is, in all its main topographical features, essentially similar to that of the surfaces of the higher surrounding tablelands and these will now be described in detail.

1. *The Bathurst Senkungsfeld.*—Owing to its gentle topography this region is frequently referred to as the Bathurst Plains. This name is, however, a misnomer, as the surface is not a plain but consists of a series of broad, rounded ridges separating moderately wide, shallow, aggraded valleys. The ridges rise to a general elevation of about 300′ above the flood plains of the valleys, and the tops of these ridges represent a peneplained surface cut out of the granite and associated strata during the earlier part of the Tertiary Period. The rock underlying this region, except for a few small areas near its margin, consists entirely of granite of a moderately acid variety; it is exceptional, however, to find outcrops of this granite in the Senkungsfeld proper neither in the stream channels nor on the ridges. Everywhere the ridges are mantled with a thick accumulation of weathered granite, while the valley floors are covered with a thick deposit of alluvium. The railway cuttings show the granite to be completely weathered to depths of upwards of 20 feet. Nowhere within the confines of the Senkungsfeld are the main streams actively eroding their channels. All the stream channels are aggraded. The whole of these features suggest an old and thoroughly mature topography.

This region is drained by the Macquarie river and its tributaries; the Macquarie river, here known as the Fish river, enters the Senkungsfeld at the south-east corner near the township of Tarana, where it emerges from a

deep valley cut into the Oberon tableland; from here it flows in a general north north-west direction in a broad, shallow valley with an extensive flood plain (see Fig. 3) until it reaches the north-western corner, where it immediately enters a gorge 1000′ deep cut into the Orange tableland. So wild and rugged is the valley of the Macquarie river beyond this point that no road follows it for any distance in this direction and to reach settlements lower down the river, one has to take a roundabout course over the Orange tableland.

The surface of the Bathurst Senkungsfeld is not definitely level but appears to be tilted upwards to some extent towards the bounding fault scarps at certain localities. In the neighbourhood of Bathurst the general level of the peneplain is 2400′ but along its eastern margin notably round about Wambool railway station, the general level is about 2550′ to 2600′.

At its south-western corner this tilting is particularly marked where the railway ascends from the Bathurst Senkungsfeld to the Orange tableland, but is quite absent further to the east, where the road from Bathurst to Rockley crosses the scarp.

Rising above the general level of the Bathurst Senkungsfeld are the Bald Hills, a group of isolated hills in the neighbourhood of Bathurst, whose highest point reaches an altitude of 2852′, that is about 500′ above the general level and 700′ above the Bathurst railway station. The highest of these hills is capped with basalt about 200′ thick and underlying this there is a bed of alluvial wash about 15′ thick, which in turn rests upon granite. These hills represent a residual of the older tableland out of which the peneplain, which forms the surface of the Bathurst Senkungsfeld, has been eroded. It corresponds

to similar residuals which occur on the Orange Tableland, such as The Brothers, 3737′ in altitude, which will be referred to in the next section. Similar basalt-capped residuals also occur, rising above the Blue Mountain Tableland, such as Mt. Tomah, Mt. King George, etc., all about 500 to 550 feet above the general peneplain level in this region.

2. *The Orange Tableland.*—This has a general altitude of about 3100′. Its surface is not flat but consists of a series of broad, mature, aggraded valleys separated from one another by well rounded ridges, the latter all rising to a general level of about 3100′. The following is a list of the trigonometrical stations occurring in the region whose altitudes are available:

Evenden	3245′
Rockley	3050′ (approx.)
Torrens	3173′
Colville	3286′
McCann	3181′
Aberfoyle	3036′
Piper	3149′
Rankin	3198′
Merrions	3222′
Wyagdon	3328′
Tambaroora	3124′

These are all on the peneplain level, some few of them rising slightly above it.

This 3100′ level represents the surface of a great peneplain, developed during the early part of the Tertiary period, not only in this region but throughout the eastern part of New South Wales. The villages of Millthorpe (3131′) and Spring Hill (3087′) are situated on this level.

Rising above this level there are some higher hills, such

as The Brothers, three isolated hills in the parish of The Brothers, the highest of which is 3737′ in altitude. Other higher points are Moorilda Trig. Station, 3502′ in altitude; Clarke Trig. Station, 3578′ in altitude; and Mt. Macquarie, 3943′ in altitude. These are residuals of an older tableland out of which the above-mentioned peneplain has been cut. Near the township of Orange is an important group of still higher hills called the Canoblas Mountains, the highest of which reaches an altitude of 4576′. These latter are not residuals of the older tableland but are a group of extinct volcanoes built up on the peneplain surface late in the Tertiary period.

The broad, mature valleys already referred to average about 300′ in depth below the tableland surface and are all well aggraded. They have been cut out of highly inclined lower palaeozoic strata as well as in places out of Tertiary basalts. The town of Orange (2846′) lies in one of these mature valleys, as also does the town of Blayney (2844′).

Mature valleys of this kind occur throughout Eastern Australia wherever undissected portions of the uplifted Tertiary peneplain still survive; they occur at all altitudes according to the amount of uplift which has taken place; they have been referred to by Mr. E. C. Andrews[1] as the "Upland Valleys," and are considered to have been formed late in the Tertiary period, before the uplift of the present tablelands.

Such streams as flow from the Orange tableland on to the Bathurst Senkungsfeld are in the higher tableland entrenched in youthful valleys. The youthful nature of these valleys changes very suddenly into mature valleys where they leave the scarp which separates the higher from the lower tableland. As already mentioned, this Orange

tableland lies to the west of the Bathurst Senkungsfeld and swings round its northern side, where it joins on to the Hillend-Hargreaves tableland, which has a similar elevation and which is in fact an eastern continuation of the Orange tableland. It also borders it on the south-western side, where it joins up with the Oberon tableland. From this latter, however, it is separated by a definite scarp, marking a change from a 3100′ elevation to a 3700′ elevation.

Throughout the Orange tableland the underlying rocks consist mainly of highly inclined Ordovician and Silurian strata, mainly slates, limestones and tuffs. These rocks, as compared with the granite underlying the Bathurst Senkungsfeld, are weak structures. Overlying these lower palaeozoic strata there is in places, particularly round about the town of Orange, a thin veneer of Tertiary basalt 200′ to 300′ in thickness.

3. *The Mt. Lambie Tableland.*—This lies to the east of the Bathurst Senkungsfeld and has a general elevation of about 4100′. The following are some of the trig. stations in this region: Mt. Lambie, 4219′; Mt. Tarana, 4178′; Ovens trig. station, 4164′. The rocks in this tableland consist mainly of lower palaeozoic strata of Silurian and Devonian age, including quartzites, slates, limestones, clay stones and tuffs. There are also some considerable areas of granite, particularly round about Yetholme, part of the same bathylith which underlies the Bathurst Senkungsfeld. The Devonian quartzites are very resistant rocks, but they do not cover a very large area, and the rocks of the region as a whole are not of a resistant character. Owing to its higher elevation, particularly as compared with the Bathurst Senkungsfeld, this region has undergone considerable dissection during the present cycle of erosion,

Fig. 3.

Fig. 4.

the lower block forming a temporary base-level of erosion for the higher block, but some remnants of the original peneplain surface still remain and these display similar surface features to those of the Orange tableland. Immediately to the east of the village of Yetholme some of the characteristic "upland valleys" occur 300′ below the general level of the tableland and Tertiary basalt is found similar to that occurring near the town of Orange. Such streams as drain from this area westwards into the Bathurst Senkungsfeld are entrenched in deep, rugged gorges. This Mt. Lambie tableland is really the western margin of the Blue Mountain tableland, the whole having a definite tilt towards the east. The whole of this region will be described in more detail in a later paper.

4. *The Oberon Tableland.*—This occurs at the south-eastern margin of the Bathurst Senkungsfeld and is really a slightly down-faulted portion of the Mt. Lambie tableland (here known as the Jenolan tableland). Its general altitude is about 3700′ and its geological structure and topography are essentially similar to that of the Orange tableland.

5. *Fault Scarps.*—The change in elevation from the lower Bathurst Senkungsfeld to the higher surrounding tablelands is remarkably abrupt, the margins everywhere being marked by a steep scarp separating the lower and higher tablelands. It is suggested that these scarps are all tectonic scarps. The most prominent of the scarps is that which forms the western margin of the Mt. Lambie tableland, the latter having an altitude of about 4100′ as against an altitude of 2400′ of the Bathurst Senkungsfeld. The scarp here is not a simple one. As one travels eastwards from Bathurst there is first a very steep rise on to a bench a few miles wide with an altitude of about 3000′ (Plate I, Fig. 4). The Yetholme trig. station, with an altitude of 3157′, lies on

this bench (Plate II, Fig. 5). From here there is another very abrupt rise to the Mt. Lambie tableland. This rise is not very noticeable on the main road, because this follows a valley cut in the higher tableland. The western margin of the Mt. Lambie tableland therefore appears to be marked by step-faulting, the first fault, which might be called the Yetholme fault, having a throw of about 1000′ to the bench on which the Yetholme trig. station stands (Plate II, Fig. 6), the second one, the Wambool fault, having a throw of about 550′, the two faults having a combined throw of from 1500′ to 1600′. The narrow bench between the Wambool and Yetholme faults has been very much dissected (Plate I, Fig. 4) and in places has been very largely removed, particularly where the main streams emerge from the Mt. Lambie tableland on to the Bathurst Senkungsfeld. In some places, notably near Wambool, large valleys have been cut along the line of the Yetholme fault and have thus partly isolated the lower 3000′ bench from the higher Mt. Lambie tableland.

The scarps which mark the junction of the Bathurst Senkungsfeld with the Orange tableland, although not so high, are just as pronounced and are probably also due to faulting, the throw of the fault here being about 700′. It is quite possible, however, that along this western margin warping may have taken place to a considerable extent, as has previously been pointed out in the south-western corner where the railway line ascends the scarp, so that the scarp here may be due to (*a*) faulting (*b*) monoclinal folding, or (*c*) a combination of both; whichever of these is correct, the fact remains that the scarp is primarily a tectonic one.

At present the writer can present no direct geological evidence of the existence of these faults. Owing to the

Fig. 5.

Fig. 6.

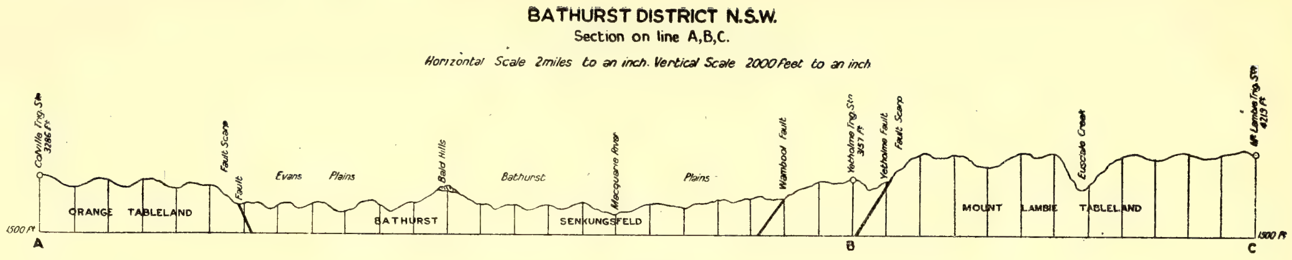

Fig. 2.
East-west section across the Bathurst Senkungsfeld.

complex geological structure, such evidence could only be obtained by the preparation of a detailed geological map of the whole region and the existence of these faults is suggested therefore from purely physiographic evidence.

If this suggestion with regard to faulting is correct then the Bathurst region is a typical Senkungsfeld or "Sunk Land," as originally suggested by Mr. E. C. Andrews.[2] It is not suggested, however, that it actually subsided but that during the elevation which brought the present tablelands into existence this particular region lagged behind during the uplift and was therefore not uplifted to such a great height as the regions immediately surrounding it. The absence of lake-deposits on the lower block indicates that the differential movement must have been a relatively slow one, the Macquarie river cutting down its gorge in the Orange tableland block as fast as the latter was elevated with respect to the Bathurst block. The physiographic evidence in support of the faulting is as follows:

a. The topography of the surface of the Bathurst Senkungsfeld is in a similar stage of development to that of the higher surrounding tablelands.

b. While active erosion is being carried on by all the main streams in the surrounding tablelands, no such erosion is taking place to-day by these streams where they cross the Bathurst Senkungsfeld.

c. The streams which enter the depressed region have youthful valleys in the higher blocks and the Macquarie river, where it leaves the depressed region, leaves it by means of an almost impassable gorge; within the Senkungsfeld itself, however, the valleys of all the streams are thoroughly mature, the main stream channels being heavily aggraded; this is particularly the case with the

Macquarie River itself, which has extensive flood-plains in the neighbourhood of Bathurst.

d. The scarps which separate the Bathurst Senkungsfeld from its surroundings are exceedingly steep and abrupt. They follow fairly straight courses, and no spurs extend from them into the lower region.

e. These scarps all display a very youthful topography as compared with the surfaces of the tablelands above and below them.

It might be argued that this relatively low-lying region is due to differential erosion in weaker rocks. In the authors' opinion the granite underlying this depressed region is not a weak structure as compared with the geological structure of the surrounding tablelands; but is relatively resistant. In the higher tablelands, notably the Mt. Lambie Tableland, there are some belts of very resistant quartzites, but these latter are quite limited with regard to the area they cover as compared with the very extensive development of weak Ordovician and Silurian rocks (mainly slates), which occupy the greater part of the surrounding tablelands. Some parts of the scarp on the eastern and north-eastern sides of the depressed region consist of the same granite as underlies the Bathurst Senkungsfeld, and it extends for some distance back into these higher tablelands. Where this granite occurs on the sides of the higher tablelands, as, for example, from Yetholme to Tarana, outcrops are numerous, whereas such outcrops are exceedingly rare in the lower depressed region, and in this depressed region the granite is everywhere very deeply weathered.

Dr. W. R. Browne[3] has suggested that, under conditions of low physiographic relief, deep and thorough decomposition of the surface rocks may be effected in the case

of such igneous rocks as granite to depths of 400′ or more, whereas this action would not take place to any notable depth in the ordinary sedimentary rocks. He states—

> "If now we imagine a region, which has for long been in the last stages of a cycle of erosion, to undergo uplift so that the peneplain or low-level region of very mature typography and of heterogeneous rock composition becomes a plateau, the new and the rejuvenated streams will attack the more deeply and thoroughly decomposed rock masses, leaving the less decomposed masses in relief. The differential rate of erosion is thus at first dependent not on the relative resistance of the various rock units to mechanical weathering and erosion so much as on the differential yielding to antecedent deep weathering."

He states further—

> "If we now take the case of a chemically weak but mechanically resistant rock like granite, during the uplift following peneplanation, it would rapidly erode to the lowest level of decay, that is to its former water-table level. Thereafter erosion of the granite, though not entirely stopped, would proceed with extreme slowness and a kind of temporary base level of erosion would be established."

Could such a process as this account for the physiographic features of the Bathurst district? What the present writer has called the peneplain level of the Bathurst District is here 700′ below the corresponding level of the Orange Tableland, so that we would have to assume that, just before the uplift which produced the present tablelands, the granite over the Bathurst area was decomposed to a depth of at least 700′, but as no solid granite has been exposed at the present time even in the base of the existing stream channels, which are 300′ below the peneplain level, the depth of decomposition of the granite would have had to be at least 1000′, which seems to be an unwarranted assumption in this particular case. A deep valley has been developed in the granite of the higher Mt. Lambie Tableland by Solitary Creek, one of the tributaries of the Macquarie River, during the present cycle of erosion, i.e., since the peneplain was up-

lifted; but this valley is no more mature than the valleys of other tributaries of the Macquarie River, cut out of the sedimentary rocks of the Orange Tableland. In both cases the surface of the Bathurst Senkungsfeld is acting as a temporary base level of erosion for the tablelands drained by these streams.

Differential erosion of the nature suggested could not explain, in the writer's opinion, the wonderfully regular system of mature ridges and "Upland Valleys" developed on the surface of the Bathurst Senkungsfeld, which so closely parallel those on the adjoining Orange Tableland, 700′ higher, and which also compare just as closely with similar features on the granite tablelands of other parts of New South Wales where the peneplain surface is still undissected.

The fact that the borders of the Bathurst Senkungsfeld to a very large extent correspond to the boundaries of the Bathurst granite bathylith would seem to indicate that the junction of the bathylith with the surrounding sedimentary rocks was a line of weakness, and that during the uplift which produced the present tablelands, the bathylith as a whole tended to lag behind, displacement and consequent faulting taking place along the junction.

As compared with other Senkungsfelder, the Bathurst example is somewhat unusual both with regard to its shape and its actual size; as previously stated, it measures about 22 miles by 19 miles, and is therefore nearly square in shape. With regard to size, some smaller examples occur in the United States as described by W. M. Davis.[4] One of these is Deep Spring Valley in the Inyo Mountains on the border of the States of California and Nevada; its dimensions are 12 miles by 5 miles, and its surface is from 1000′ to 3000′ below that of the surrounding highlands.

Another example is the Salina Valley in the same region, which measures 25 miles by 10 miles, the mountains on one side of its rising 6000′ above its surface.

The Sydney Senkungsfeld of New South Wales is somewhat larger, its dimensions being about 40 miles long by 20 miles wide.

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Explanation of Plates.

Plate .I

Fig. 3.—Valley of the Macquarie River at Bathurst. The ridge in the middle distance rises 300ft. above the flood plain. The Mt. Lambie tableland is faintly shown on the sky line.

Fig. 4.—View looking east from the Bathurst Senkungsfeld towards the Mt. Lambie tableland. In the foreground are the mature valleys and ridges which characterise the surface of the Bathurst Senkungsfeld. In the middle distance is the 3,000ft. bench partly dissected. In the background is the fault scarp which forms the western margin of the Mt. Lambie tableland.

Plate II.

Fig. 5.—View of the Mt. Lambie tableland looking north-north-east from the Bathurst-Tarana road. On the sky line

to the left is the 3,000ft. bench, and to the right the higher Mt. Lambie tableland.

Fig. 6.—The Yetholme fault scarp immediately to the north of the Bathurst-Yetholme road.

ON A SPECIMEN OF FOSSIL TIMBER FROM THE SYDNEY HARBOUR COLLIERY.

By R. T. Baker.

With Plates III-VI.

(*Read before the Royal Society of New South Wales, Aug.* 5, 1931.)

Introduction.

This specimen was discovered by Mr. D. Scully in this mine in 1898 at a depth of 2,225 feet, and noticing distinct, white markings radiating from the pith, much resembling medullary rays, he was under the impression that it was an "Oak"—a vernacular name applied in Australia to the species of the Genus *Casuarina* of the Natural Order, Casuarineæ. A microscopical examination showed, however, that these white markings are due to the presence of calcium carbonate as explained below.

The attention of the author was drawn to it by an article written by Mr. Scully on fossils, in which he referred to this "find" under the name of "Oak," and states that when he arrived at the surface the whole specimen had been appropriated.

At the time of the "find" Mr. J. L. C. Rae was the manager, and he procured a piece, which he very kindly presented to the author, in order that a scientific investigation might be undertaken, and for which kindness the author herewith expresses his gratitude. However, sufficient sections for microscopical examinations were obtained without destroying the facies of the specimen, leaving two-thirds of the original complete in the circumferential area.

Mr. Rae states that "it was found in a band of hard, greenish, micaceous sandstone which extended from a depth of 2,219 feet to 2,322 feet; the broken off ends remaining in the wall of the excavation on each side of the shaft at practically its full diameter, so that the total length of the fossil stem procured was about 20 feet."

Its original shape is excellently preserved, showing that it had not been subjected to any crushing strain, or if it had, the coating of calcium carbonate had enabled it to resist such pressure.

General Description of the Specimen.

The piece of fossil timber upon which this research is founded, was sawn off when the log came to the surface. It is almost circular in form, measuring in the longer axis $3\frac{1}{4}$ inches, and in the shorter one, $2\frac{3}{4}$ inches, and $1\frac{1}{2}$ inches in thickness (Plate III., Figs. 1 and 2). Both faces had been polished. In Fig. 1 it is shown in perspective, whilst Fig. 2 gives a front view of the transverse section showing the two kinds of material of which it is composed, viz.: the dark, black, inner portion, being the fossilized timber, and the outer, pale coloured band composed of calcium carbonate.

No bark has been preserved; the black substance on the outer edge is not that material, but portions of tracheids displaced by the calcium carbonate. The pith is not in the centre of the wood, but its position is indicated by the small white spot towards the upper left of the centre; the annual rings are not seen in this surface. The rings of white spots are calcium carbonate in the tracheids, or canals in transverse section of this substance.

No oil or turpentine cells, canals, channels or passages were found throughout the xylem material examined.

That portion of the wood between the nearest part of the circumference and the pith, represents the slow growth of the stem, whilst in the opposite axis to this, the quicker growth, due to the external conditions of cold and warmth respectively. From this view of the specimen it is seen that the calcium carbonate deposit is most pronounced on the cooler side of the tree's environment, and gradually peters out at the extremities exposed to the warmer conditions that prevailed during the life of the tree. The same substance occurs in the pith.

To the top, left and right of the pith (Plate III., Fig. 2), are shown two white radial lines; these are channels conveying the calcium carbonate from the vertical canals of the xylem, to be deposited on the exterior of the stem, in the form of columns seen in transverse sections (Plate IV, Fig. 3), in which figure can also be seen to the right and also lower left of pith, rays filled with calcium carbonate.

Description of the Timber Structure.

This portion of the specimen is particularly well preserved, scarcely an organ of structure being wanting to enable it to be systematically described. The central column or pith has almost entirely been replaced by calcium carbonate, and only a few spiral vessels and parenchyma tissue have been preserved in that part of the stem or primary xylem and in juxtaposition to that mineral. Xylem parenchyma is entirely absent.

(*a*) *Transverse Section.*

The tracheal structure is uniform throughout the primary and secondary xylem area.

The annual rings are well marked (Plate IV., Fig. 3, and Plate V., Fig. 5), the dark autumn growth being quite prominent, and producing a distinct line of demarcation

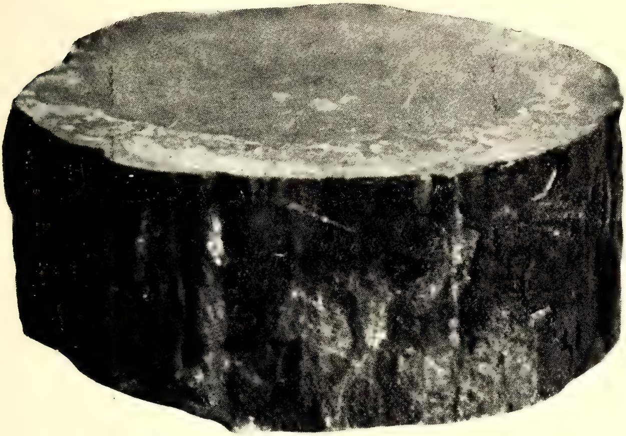

Fig. 1.

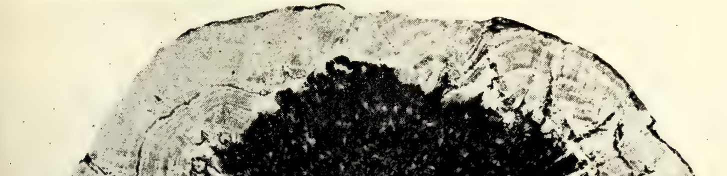

Fig. 2.

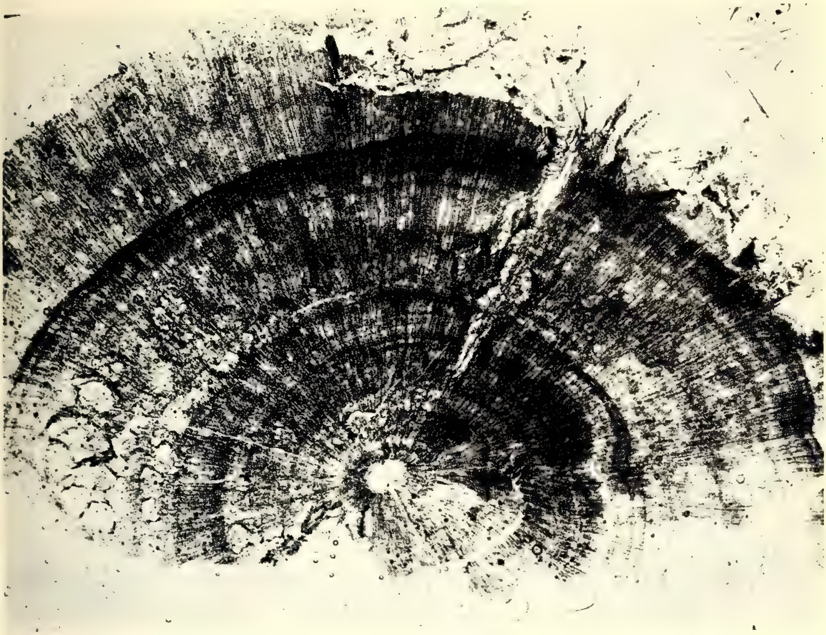

Fig. 3.

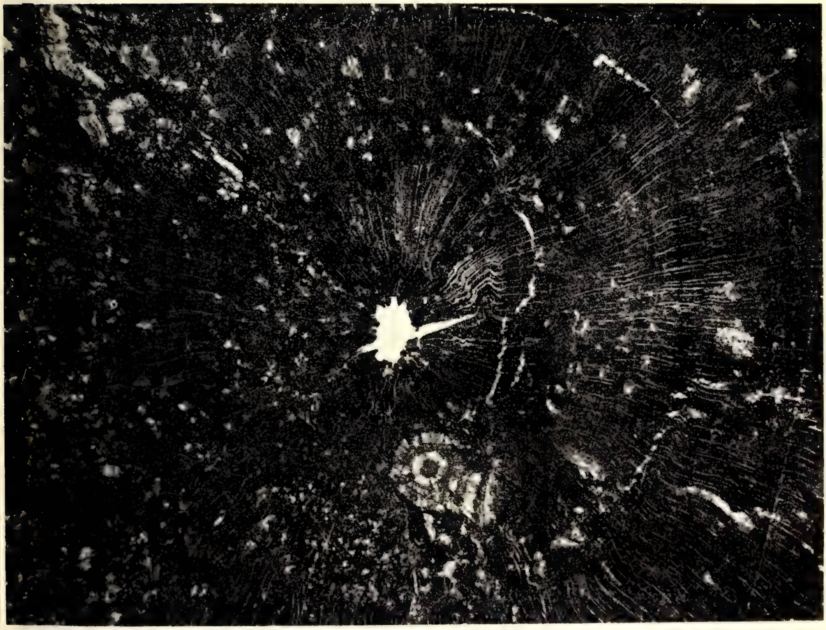

Fig. 4.

between it and the spring growth, and these number about six—the approximate age of the tree—the two outer ones being half an inch apart, thus indicating that the tree was a rapid grower for its age, and height of stem. The others gradually lessen in width towards the centre, whilst one or two seem to peter out and so do not complete the circle.

The medullary rays are very numerous, fine, and more often than not, are filled with calcium carbonate, and so probably acting as ducts to convey that substance from the pith to the vertical channels or to the outer surface of the stem.

The tracheids as seen in section, show great variety of shape, ranging from triangular to circular or rectangular, but mostly are irregularly hexagonal or pentagonal. The rows of tracheids vary in number between the rays, from a few, up to 25 or even over 30. Only in just a very few tracheids was a very pale brown deposit detected (vide remarks under radial section).

(*b*) *Radial Section.*

The medullary ray parenchyma, like the rest of the structure, is well preserved, and is characterised by thin walls in which, on the radial surface, are pitted cells varying in number between each tracheid, but mostly there are two of these cells, with an oblique slit.

On the radial walls of the tracheids, are well formed and prominent bordered pits, in all instances in uniseriate rows the full width of the lumen, circular in shape, not adpressed, and with a circular depression in the centre. No bars of Sanio were seen. This feature is in accord with what obtains in the Australian Genus *Callitris*, and so, in this feature at least, shows no connection with the Australian Genera *Araucaria* and *Agathis*. They can be seen in Plate V., Fig. 7, and more prominently so in the more

highly magnified Plate V., Fig. 8. In the centre of Plate V., Fig. 9, the walls of the tracheids appear to be broken, but this feature is due to bordered pits on the tangential walls being cut in section.

These bordered pits occurring in the tangential walls (Plate V., Fig. 10), are a very unusual feature in Conifers.

(c) *Tangential Section.*

The end-on view of the medullary rays (Plate V., Fig. 10), shows how numerous they are. All are uniseriate, varying in number of divisions from a few up to a dozen or more, and generally are filled with calcium carbonate. The unique feature of this section is the presence of uniseriate rows of bordered pits in the tangential walls similar to those shown in Plate V., Fig. 8.

Calcium Carbonate.

As stated above, in a cross section the specimen is seen to consist of two well defined substances, i.e., the black part comprising the fossil timber, and the outer, broad, light coloured band composed of a number of well defined concentric accumulations.

An analysis of this material, as given below, showed that it is almost completely composed of calcium carbonate.

Calcium carbonate	96.000%
Magnesium carbonate	0.005%
Oxides of Iron and Aluminium ..	3.720%
Silica	0.268%

Nor is it restricted to the exterior of the wood, but is found also to permeate or occur in the pith channels or canals radiating from this centre through the xylem to the exterior surface (Figs. 2, 3, 4, 12, 13), and also in vertical canals of varying diameters, and it is from these that the exterior deposit of calcium carbonate obtained its supplies.

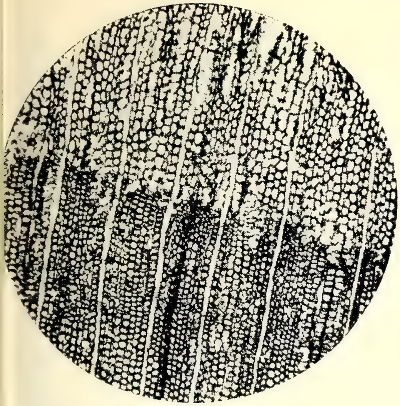

Fig. 5.

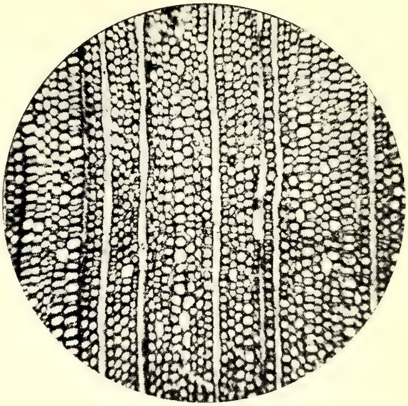

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

Fig. 12.

Fig. 13.

Fig. 14.

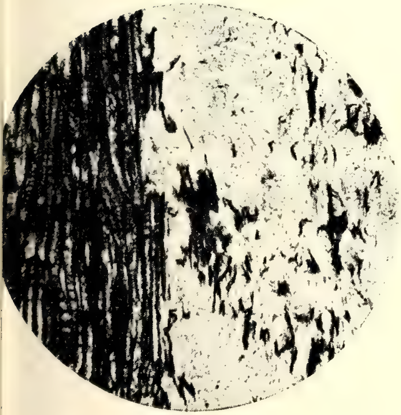

Fig. 15.

Fig. 16.

In Plate III., Fig. 2, and Plate IV., Fig. 4, it is shown to occur as small white spots in concentric circles around the pith, and on a high magnification shows a coalescence, and thus forming portions of a ring. Plate IV., Fig. 3, shows a number of vertical canals of calcium carbonate, connecting with a horizontal canal conveying this mineral to form a concentrically built column at the top right outer edge of the xylem, and in so doing, it may be noted that it has pushed out at least two or three rows of the tracheids of the last annual ring. The one on the right is displaced very much more so. Just above the pith are three smaller vertical canals in section, and to the left of the pith is a cluster of these, the inner ones forming a ring.

This plate also shows the well defined annual rings. Plate III., Fig. 2, illustrates a cluster in cross section of the concentrically built columns of calcium carbonate on the exterior surface of the stem, the curved narrow black bands removed from their centres are displaced xylem tracheids, whilst Plate VI., Fig. 15, shows in the centre a cluster of removed tracheids producing a tessellated effect.

Plate VI., Fig. 13 shows a transverse section of a vertical canal with calcium carbonate as it was received from the tracheids, the central supply being indicated by the radiating lines, from the two rows of compressed tracheids which very much resemble the transfusion tissue which supplies silica to the leaves of Dicotyledoneous plants. The dark boundary is composed of displaced tracheids. Plate VI., Fig. 14, is a vertical section showing that these features are truly canals—the whole of the white body.

These exterior columns of calcium carbonate are eventually backed by a mass of crystalline carbonate of lime, in which also are found detached pieces of tracheids (Plate III., Fig. 2, and Plate VI., Fig. 15).

Now, in view of Newton's statement in his Principia Rule I. . . . "That Nature does nothing in vain," one naturally asks, then, for what purpose or object was this substance built up by the tree, for it would be put there to serve some object in its life history.

One is hardly justified in looking upon it as a valueless, physiological structure, but rather as one of great importance to its very existence.

Warming, in his "Etudes sur la famille des Podostemaceæ"—plants of which Natural Order all grow in swiftly flowing rivers and streams, and which, therefore, require to be specially protected against the shearing action of the violently agitated water, believes that Silica cells and Silica corpuscles play a mechanical part in the life of plants of this Natural Order.

It is universally accepted that the Coal Measures were laid down in water—stagnant most probably— and as this tree coated itself with calcium carbonate it may perhaps be inferred that it grew at the inlet or outlet of such water, and thus had to provide itself with a mechanical contrivance to resist "the shearing action of the running water" just as in the case of the Podostemaceæ.

And this plan of construction is further supported by its regularity and design for strength, by building this supporting "wall" in columns, and these again protected by an outer layer with a comparatively smooth surface, and so deflecting the oncoming water, or to withstand adverse external climatic conditions.

Man to-day has produced a replique of this handiwork of nature, for the engineer builds similarly when constructing the ends of wharves exposed to heavy seas and gales, little thinking that nature anticipated his designs untold ages ago.

Traumatic deposits they cannot be, for these are laid down without any order or system—just a jumble of exuded substances, as for instance, Kino and Resin.

One can hardly imagine it as a waste product as in the case of calcium oxalate crystals found in the wood of some Dicotyledoneous woods.

This tree had a further physical weakness in that the tracheids would be frail, having bordered pits on both radial and tangential walls—perforations not conducive to strength.

In addition to giving the tree strength, it also served another purpose—protecting it against cold weather conditions, for it is on the side exposed to such that it has its greatest thickness.

Nature has provided the non-Conifers-Dicotyledons, with an organ which serves the mechanical purpose of giving the tree strength, and so in that case there is no necessity to call in the aid of an extraneous substance.

That it was traumatic can hardly be entertained, for it surrounds the whole stem, and also that it was supplied by channels deeply set in the xylem of the annual rings, and even direct from the pith itself. Further, had it been a wound right round the stem it would have had an injury equivalent to the modern method of "ringbarking" a tree, and so died before so heavy a deposit could have been completed.

Manganese Compound.

A reference is made above of the occurrence of a light brown coloured substance in the tracheids (Plate V., Fig. 6). Now this is the manganese compound first recorded as occurring in the wood of Australian living Conifers by Baker and Smith in "Pines of Australia." In the many instances of its occurrence, illustrated in that work, it is

always shown as long, cylindrical deposits in both the tracheids and ray parenchyma, but in this wood it occurs in the tracheids only, and as small spherical bodies. This is the first instance, as far as the author knows, of its ever having been recorded in this shape, and further, this is also the first record of this substance occurring in a fossil timber. They are shown in a central tracheid in Plate VI., Fig. 11.

It is quite possible that these indicate a very ancient ancestral feature.

Discussion.

The histological characters are so well preserved in the specimen that no difficulty was experienced in systematically placing it as of Gymnospermous origin.

Its homogeneous structure was helpful in working out its differences, affinities, and similarities, from or to described species of fossil timber by the various palæontological authors.

No attempt was made to place it under the heading *Dadoxylon,* a too comprehensive term, in the Author's opinion, in view of our present extensive knowledge of living Coniferous timbers, and was proposed, so the Author was informed, "to include wood having pitted ducts where the wood *may be* equally of the Cordaitean or Coniferous type."

It cannot be placed with the *Cordaites,* for as Scott states (New Phytologist, Vol. I., 1902), "they are anatomically on the same level as recent Cycads"—a group of plants with which this fossil specimen has little or no connection in its structure, nor has it crowded bordered pits as obtain in that group of plants.*

* Jeffrey: Anatomy of Woody Plants, p. 289, pl. 22 & 48.

Again, Scott, in his work "Extinct Plants," p. 149, states: "In the lower Carbonaceous Flora all traces of Cycads are absent, and it is probably from this geological area, in view of the chemical analysis, that the fossil specimen of this paper belongs. Further, the disposition of the bordered pits and other features differentiate the Sydney specimen from the *Pitae, Cupressinoxylon* and *Cedroxylon.*

Amongst modern Conifers it certainly differs from *Araucaria* anatomically, and in this respect also from *Dacrydium, Podocarpus* and *Agathis.*

Its nearest affinities are with the Genus *Callitris,* both in the arrangement of the bordered pits, nature of tracheids, ray parenchyma, annual rings and presence of the manganese compound, as well as the entire absence of oil canals.

The presence of the calcium carbonate, on the outer surface and in the wood texture, has never yet been recorded as occurring in the wood of any living *Callitris* nor any Australian Conifer. Amongst these, its wood structure more closely resembles that of *Callitris arenosa,* a native of the North Coast of N.S.W. and Southern Queensland.

The presence of the calcium carbonate would appear, according to Geikie and other authors, to place it geologically as from the Lower Carboniferous series, and if this determination be correct, then, according to Scott, *loc. cit. supra,* p. 150, true Conifers have not been previously found, then this Sydney specimen is probably a record of a Conifer from that period.

Seward, in his Fossil Plants, 1917, Vol. III., figures and describes a Coniferous species founded on a specimen obtained from the Priestly Glacier by the Northern Party of Captain Scott's Second Antarctic Expedition, and gives it generic and specific rank under the name of *Antarcticoxylon Priestleyi.*

Now, in comparing the Sydney specimen plates and description with this species it is very noticeable how many features these two specimens have in agreement. Seward states that his specimen was imperfectly preserved (compressed), and so the *primary* xylem is too imperfect to admit of any satisfactory comparison as regards this tissue with other types, and this remark applies to the Sydney specimen; however, almost all the other features are similar, or at least appear so, notwithstanding its having been distorted out of its original protundity. Its chief difference appears to be that it is "a silicified stem," which the Sydney specimen is not, and also having double as well as single rows of pitted cells. "Only single rows were found in the sections examined, although other parts may have double rows," but judging from the diameter of the tracheids, it is very doubtful. Medullary rays are identical in both cases, as well as the secondary xylem.

In describing his species, Professor Seward states: "An interesting feature seen in transverse section of the secondary wood is the occurrence of light bands concentric with the rings of growth, which are broadest near the long axis of the stem. In their narrowest parts these bands are clearly due to partial destruction of the secondary tracheids."

Now that fairly well describes a similar phenomenon in the Sydney specimen, Plate III., Fig. 2, Plate IV., Figs. 3 and 4, for those "bands" or rings correspond to similar rings in the Sydney species, but in this case (seen macroscopically), are composed of separate white bodies, and yet microscopically they are seen in places to be continuous or coalesce, and so perhaps continuity in the Antarctic specimen may possibly be due to the compression to which the specimen had been subjected during the past ages. In

Plate IV., Fig. 3, the substance of which these rings is composed is seen coalescing, and thus forming a ring.

In Plate III., Figs. 2, 4, Plate IV., Figs. 3 and 4 of this paper are shown channels extending from these canals conveying the calcium carbonate to the outer surface of the stem, and similar features are shown to the left and top in Seward's figure (loc. cit.).

If Professor Seward had had a more perfect specimen upon which to work, it would probably have been found that what are thought to be leaf traces would prove to be silica channels corresponding to the calcium carbonate channels in the Sydney specimen and the "crushed parenchyma tissue" referred to as "traumatic" may possibly be tracheids detached by the silica, for they very much resemble in character and disposition those found in the Sydney specimen.

Like the Antarctic fossil, the Sydney one is wanting in bark.

As these two specimens have thus several specific features in common, the Sydney specimen has been systematically placed in the Genus *Antarcticoxylon,* with the species name of *Raei,* after Mr. J. L. C. Rae, to whom the author is so much indebted for the specimen upon which this investigation has been carried out.

As the geological age of the Antarctic specimen is not known definitely, it may eventually be found, in view of so much agreement in structure, as now shown to exist in the two, that they are of the same period. The main difference between the two is the presence of silica and calcium carbonate respectively in each.

It is well known amongst geologists that fossil plants and their parts are often found incrustated, and their parts permeated with calcium carbonate, which acts as a pre-

servative, and sometimes forming a perfect cast of the plant, the presence of this substance being attributed to the influence of water saturated with calcium carbonate.

Whilst this latter may be true in some cases, yet the author is of opinion that in some instances it is present in excess in the soil, in which case it is broken down by the root hairs and passed into the plant structure for the purpose of (1) building up the cell walls, and (2) encasing the tree for self preservation, and these two are illustrated in the Sydney specimen.

Under no circumstances is the author prepared to admit that it is a valueless structure—in fact, nothing is a valueless structure in nature, and further, if the tree didn't need it, the root hairs would not absorb it.

In this case one sees a splendid system of mechanism, all the parts of the tree working as a machine, in order to triumph or overcome adverse conditions of environment.

It is generally thought that the calcification and silicification of fossil wood takes place after the tree has died, but it is difficult in this case to understand how such took place after the tree was dead, for then the root hairs were dead also, and so could not function, that is, dissolve the calcium carbonate and pass it into the tracheids, displacing the cellulose (if such existed) of the walls, and substituting the carbonate of lime, and further, depositing it in the outside of the tree.

Then one is faced with the mystery as to why nature does not let the wood decay or rot, and so be saved all this labour, for as far as we know, this preserving of the timber serves no purpose in nature, and also whence comes the mechanical power which forces the calcium carbonate through and through the whole wood structure, if the root hairs are dead?

As stated above, the calcium carbonate is not evenly distributed on the exterior surface of the tree, being far more heavily deposited on one side than the other, a circumstance which well illustrates Rule I. in Newton's Principia:—"Nature does nothing in vain, and *more* is vain when *less* will serve," and so *more* is required in this case to resist adverse climatic conditions, and *less* "*serves*" on the side facing the sun.

Turning from the pointer-readings, and concentrating on what can only be inferred by the mind to explain this arrangement of calcium carbonate by nature, one wonders whether this deposit in the tree indicates a period in arboreal life when trees had no bark—a material later introduced perhaps by nature to protect the new internal structure and tender Cambium, for this latter appears to be absent from fossil trees.

It may be mentioned that amongst living trees, the bark of "Grey Mangrove," *Avicennia officinalis,* as such, is negligible, there being no cambium to protect, but in order to resist the shearing action of the water of tidal rivers, nature builds the stem with a ply structure—the only one of its kind in the whole botanical world. (Vide paper by the author, *Roy. Soc. N.S.W.,* Vol. XLIX, 1915).

In conclusion, one may quote the words of Professor Judd: "We still regard fossils as the medals of creation—representing periods like ancient coins."

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Explanation of Plates.

Plate III.—

Fig. 1.—A perspective view of the specimen of fossil timber from the Sydney Harbour Colliery. Nat. size.

Fig. 2.—An end view of above. The light coloured portion is calcium carbonate. Slightly enlarged.

Plate IV.—

Fig. 3.—Upper portion of Fig. 2. The annual rings are clearly defined, the darker circles marking the autumn growth, the lighter areas the spring growth. To the left, the clusters of circular bodies are calcium carbonate canals and from the pith is seen a horizontal channel extending to the outer surface of the stem. Medullary rays are seen to be very fine and numerous. X2.

Fig. 4.—Structure surrounding the pith more highly magnified. The body below the pith is not a leaf trace but a calcium carbonate canal. X3.

Plate V.—

Fig. 5.—Transverse section through portion of the timber. The dark area of tracheids marks the autumn growth of an annual ring, the lighter upper portion, the spring growth. X40.

Fig. 6.—Transverse section through spring growth, showing the variation in the number of rows of tracheids between the rays—white lines filled with calcium carbonate. In a few tracheids, manganese compounds can just be detected. X40.

Fig. 7.—Radial section showing (1) uniseriate rows of bordered pits in centre tracheids, (2) rays with simple pits and absence of Abietineæ markings. X35.

Fig. 8.—A higher magnification of Fig. 7, showing more clearly the bordered pits and simple pits in the ray parenchyma. X40.

Fig. 9.—A radial section showing how the tracheid tangential walls are weakened by the numerous bordered pits (in section). X40.

Fig. 10.—A tangential section showing bordered pits on tangential walls and end-on view of rays mostly filled with calcium carbonate. X50.

Plate VI.—

Fig. 11.—A radial section showing on centre tracheid black spherical bodies of the manganese compound, a unique form, as it usually occurs in a continuous body. X40.

Fig. 12.—Transverse section showing shape and contour of pith and surrounding primary xylem. X35.

Fig. 13.—A transverse section through a vertical canal, showing how calcium carbonate is discharged into it from a few rows of tracheids (see also bottom Fig. 3) much resembling the transfusion tissue of Angiosperms. The black band surrounding the calcium carbonate is composed of displaced tracheids. X40.

Fig. 14.—Radial section through a vertical canal of calcium carbonate, showing xylem structure on each side of it. X40.

Fig. 15.—On the right, a mass of calcium carbonate with displaced tracheids scattered throughout this substance. X40.

Fig. 16.—A higher magnification of the outer edge of the calcium carbonate shown in Fig. 15.

NOTES ON BATHYLITHS AND SOME OF THEIR IMPLICATIONS.

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Introduction.

The term *bathylith* was originally employed by Suess[1] to signify large masses of plutonic igneous rock, which, he believed, were cake-like in form, and filled preformed open spaces in the earth's crust. Later he assumed for them a shape and a mode of origin which postulated their extension downwards to unknown depths.

Since Suess' time very varied conceptions of the origin, mode of emplacement and shape of these masses have been expressed by different geologists. Daly[2] has devoted considerable attention to these matters, and has endeavoured to give more precise significance to the term by summarizing the general characteristics of bathyliths and by assembling and describing maps and sections of a number of such intrusions. A consideration of the examples cited by Daly and others makes it clear that there have been grouped under one general heading intrusive masses differing from each other in many respects, and evidently brought into position under very different circumstances; and from time to time indications have been forthcoming that investigators have been in doubt as to the propriety of describing certain intrusions as bathyliths.

Adams and Barlow[3], following Lawson, used the term in connection with their Haliburton-Bancroft work "to designate great lenticular-shaped or rounded bosses of granite or gneiss, which are found arching up the overlying strata through which they penetrate, disintegrating the latter, and which possess a more or less distinct foliation, which is seen to conform in general to the strike of the invaded rocks when these latter have not been removed by denudation."

Some authorities are opposed to the description of rock-masses like these, which exhibit concordant instead of cross-cutting relations towards the invaded formations, as bathyliths; nevertheless there seems on the whole a general tendency among geologists to describe under this head all large plutonic intrusions, whether transgressive or not, which are of such dimensions, and whose field-relations are such, as to prohibit their classification as sills, laccoliths, dykes or similar types. Since there is no agreement, and little prospect of agreement, about the shape and underground relations of bathyliths, and since indeed these may vary in different cases, it is best in the present state of our ignorance to exclude any particular connotation as to shape, relations to invaded rocks, or mode of emplacement from the use of the term.

In a posthumous paper by Barrell[4] a useful distinction is drawn between orogenic and plateau bathyliths, the former comprising those which are associated with regionally-metamorphosed sediments and have been injected under conditions of tangential or horizontal compression, the latter those that have been injected at a time when vertical crust-movements were dominant.

In a later paper by Billings[5] these types are referred to as synchronous and subsequent bathyliths respectively,

these descriptions having reference to the contemporaneity or otherwise of intrusion with orogenic epochs.

According to Balk[6], German geologists distinguish between gneissoid granites, which appear as elongated masses parallel to the regional trend, and granites proper, which exhibit cross-cutting relations. These differences in behaviour are regarded as significant; they have been interpreted by Professor Cloos in a paper which, unfortunately, is not available to the present writer. Balk, apparently, does not consider the masses of gneissoid granite as true bathyliths.

The recognition of two main bathylithic types according to the tectonic conditions prevailing at the time of injection is extremely important and very necessary, since, while all bathyliths appear to be associated in time with mountain-building epochs, as Daly has observed, there is plenty of evidence that the actual conditions attending the injection of the magma may differ very materially, and the differences are reflected in the external relations and internal characters of the intrusive masses.

The necessity for distinguishing two main types of abyssal intrusion having become apparent, some revision of Daly's summary of characteristics is called for.

From a study of some of the pertinent literature, and from the examination of a number of both synchronous and subsequent intrusions in this State and elsewhere in Australia, the author is moved to put forward some generalizations with regard to them.

Characters of Synchronous Bathyliths.

Synchronous bathyliths generally show all or most of the undermentioned characteristics:—

(a) There is constant association with schists or other regionally-altered and highly-folded rocks.

(b) Boundaries are steep or vertical in section, in plan parallel or sub-parallel with the strike of the enclosing rocks but often ill-defined through gradation from the invading into the invaded rock; outcrops are markedly elongated parallel to the axis of folding, and peripheral lenses may be numerous.

(c) The roof is highly irregular, tending to fray out into sills and parallel lenses and tongues.

(d) Gneissic structure is commonly developed in the igneous rock, either primary alone or primary and secondary, the banding or foliation being parallel to the boundary of the intrusion and sometimes varied with minor crinkles and contortions.

(e) Abundant pegmatite is generally present, both as peripheral *lit-par-lit* injections and within the mass as contemporaneous stringers and as definite dykes.

(f) Inclusions are common, elongated parallel to the walls and the gneissic banding, and not deorientated.

(g) No hornfelsing of the country-rock has occurred, though this may have suffered much alteration through impregnation (granitization).

(h) There is little or no indication of serial differentiation in the intrusion, but pegmatite and gabbro dykes may appear, possibly as complementary differentiates; dynamic differentiation through squeezing out of residual magma may also be apparent.

(i) Minerals like andalusite, sillimanite, cordierite, garnet and epidote may be present in the granitic igneous rocks, either through contamination or as primary crystallizations. Some local modification of the granite through incorporation of country-rock may occur.

Characters of Subsequent Bathyliths.

The following are the chief contrasting characters of subsequent bathyliths:—

(a) No necessary association with regionally-metamorphosed rocks is observed; the country rock may be only moderately folded.

(b) Boundaries are mostly sharp, and cross-cutting relations general, though there may be local concordance with the enclosing strata; outcrops are irregular in plan. Peripheral lenses are absent, but there may be dyke- and sill-apophyses.

(c) Indications may point to the roof having been fairly flat, or irregularly domed.

(d) The granite is in general massive, though marginally it may have directive structures.

(e) *Lit-par-lit* injection is scarce or absent, and there is a general scarcity of pegmatites, except as segregation-veins, but fine-grained aplites are common, sometimes accompanied by lamprophyre dykes.

(f) Inclusions are angular and deorientated.

(g) Where the country-rocks have not suffered much previous metamorphism a contact-aureole is present, with typical contact-minerals, not usually, however, of very high-temperature formation.

(h) Extensive serial differentiation is indicated, often with evidence of more than one injection of magma.

(i) Contamination through incorporation of country-rock is not in general noteworthy.

Notes on Synchronous Bathyliths in N.S.W.

The data concerning the synchronous bathyliths in this State have been obtained mainly from a study of occurrences in the Barrier Ranges, and on the Monaro plateau

around and to the north of Cooma, as well as from a brief examination of the granite at Albury.

The first have been the subject of detailed mapping and investigation by the Government Geologist, Mr. E. C. Andrews, and his assistants[7], and a study of the maps accompanying the Memoir on the area reveals very strikingly the field-characters of the igneous intrusions. The Willyama (Archaeozoic) Series, dominantly of pelitic sediments, was highly metamorphosed and folded, and injected by granitic gneisses, with accompanying gabbros and pegmatites, probably at the close of the Willyama period of sedimentation. The granites and some of the gabbros have a marked primary gneissic structure, often with a cataclastic foliation superimposed. The sill-habit is by far the most common for both acid and basic rocks about Broken Hill, but outcrops suggesting phacoidal forms are also common, especially for the granite-gneisses, around which in places the sedimentary schists are seen to be bent. Transgressive boundaries are practically if not entirely unknown, and indeed the structures of domes and basins in the sedimentary series are indicated by the intercalated sills of granite and gabbro.

In his sections across the area Mr. Andrews makes it clear that he conceives all these linear outcrops to be parts of a few far-flung narrow parallel intrusive sheets or layers of igneous material which have taken part in the folding of the whole terrain and then been revealed by erosion; the same view is stated more or less explicitly in the text of the Memoir.

The impression gained by the author from a personal examination of much of the area, partly under the guidance of Mr. Andrews, is that the igneous intrusions as we see them to-day are substantially in the same attitudes and

orientations as when they were first consolidated, and that the magma was forced or insinuated up along pre-existing planes of weakness, during the folding of the sedimentary rocks, but after their regional metamorphism had been accomplished.

This is shown by the primary gneissic foliation of the granites, by the intimate interleaving of sillimanite-schist with granite-gneiss and by the presence in the gneiss of inclusions of schist and of metamorphic minerals derived therefrom. In the sills the foliation is generally vertical, though it may dip at low angles where there has been local buckling of the strata; in the phacoidal outcrops the planes of foliation may dip inwards or outwards at steep angles.

It is rather unfortunate that there is no dissection of the Barrier Ranges of sufficient magnitude to afford some clue as to the relations in depth between invading and invaded formations, but it appears most reasonable to suppose that the various sills and lenses connect downwards more or less directly to one or more large masses of granitic magma underlying the whole central part of the Broken Hill area, from which they were originally forced up concordantly along the bedding-planes of the altered sedimentary rocks. Indeed some of the larger roughly lenticular outcrops of porphyritic and non-porphyritic primary granite-gneiss might themselves be regarded as small synchronous bathyliths, or as protuberances from the upper portions of such bathyliths.

At Cooma, Ordovician schists with a meridional strike are invaded by two related granitic intrusions, both probably of late-Ordovician age[8, 9]. The earlier of the two appears almost entirely in the form of innumerable narrow concordant sheets or sills. The second intrusion, which is the more important and extensive, is in places massive, but

elsewhere has marked primary banding. It makes a continuous outcrop in and about the town, and to the east its boundaries are more or less sharp, but to the west away from the main mass there are abundant narrow sills and lenses of gneiss or granite. The solid outcrop also frays out into tongues and sills to the north, and these apparently join into two separate parallel sill-like masses which may be traced to a point about 15 miles north of Cooma, where they are cut off by a later intrusion in which fragments of gneiss may be recognised for a further eleven miles at least. It is inferred that the solid outcrop at Cooma is a portion of the main bathylithic mass, that the outlying lenses and sills are upward penetrations from the roof, and that the northward extensions, if they could be followed downwards, would be found to unite into one mass continuous with that exposed at Cooma.

Lit-par-lit injection of the schists by pegmatitic material is very marked at Cooma, and in addition the schists have been thoroughly soaked by magmatic fluids and granitized. At Broken Hill, *lit-par-lit* injection of the schist is not so much in evidence, possibly because of the abundant mantle of alluvium and blown sand round the igneous masses, but there is in places an abundance of pegmatitic stringers through the gneiss itself, and at the margins there may be such interleaving with the country-rock and such an apparent gradual passage from sedimentary schist to igneous gneiss that an actual boundary between them is very difficult to draw.

At Broken Hill, Cooma and Albury the presence of aluminous minerals in the granites is quite a striking feature. In the first locality little lenticular aggregates of sillimanite about a couple of inches in length, sometimes longer, often surrounded by a rim of sericite, are quite

common as marginal enclosures in certain of the more acid igneous rocks, while cordierite is a constituent of some pegmatites and aplites. The sillimanite lenses seem to be essentially similar to those described by W. J. Miller[10] as occurring included in a granite in New York State. Garnet in various stages of disruption is also found in certain phases of nearly all the granitic rocks. Of the Cooma gneiss cordierite and sillimanite are quite common and notable constituents, while sillimanite alone has been found in the Albury granite. Undoubtedly the presence of some of these minerals is due to incorporation of country-rock by the magma, though in other cases they appear to be primary crystallizations.

Another common feature of the synchronous bathyliths is the presence of marginal inclusions of country-rock which are very much elongated and have not suffered deorientation. These are not so evident at Cooma as about Broken Hill, where, along the margins and even near the centres of the granite-gneiss outcrops, there have been found these elongated inclusions of country-rock, some recognisably of sedimentary origin, but others of altered basic igneous rocks, which may easily be mistaken in the field for concordant sill-like intrusions through the gneiss. An instructive section through the granite-gneiss is to be found in a cutting on the Menindie railway-line at Broken Hill, a small portion of which is illustrated in Plate LVIII. of Mr. Andrew's Memoir. The basic rocks, here, gabbros and amphibolites, are in part no doubt intrusive through the granite-gneiss, but some would appear to be basic schists which antedate the gneiss, and which were intimately penetrated by the granite-gneiss magma during its intrusion.

In some instances it may be that the masses of country-rock which appear as inclusions owe their present orientation to their having been softened and pulled out in the

flowing magma, but in other cases it seems evident that the magma made its way by a process of "peaceful penetration," thin veinlets insinuating themselves outwards and upwards along planes of weakness in the schists, and gradually isolating very elongated masses which, though moved laterally, were moved so very uniformly that they never lost their orientation. Others again of these apparent inclusions which retain their original orientation may be really remnants of an irregular roof, like the "roof-pendants" described by Daly.

Examples of abundant orientated—or undeorientated—inclusions in granite-gneiss have been described and figured by Lacroix[11], Peach *et al.*[12], Lawson[13], Adams and Barlow[3], Fenner[14], Billings[5], Tilley[15], and a host of other workers. So abundant in some bathyliths are these inclusions in all stages of disintegration and incorporation that Foye[16] in 1916 was moved to suggest the term *stromatolith* (layer-intrusion) instead of bathylith to describe those large concordant plutonic masses in which orientated inclusions form a conspicuous feature. The name does not appear to have come into general use, possibly because it tends to over-emphasize the part played by the layers of sedimentary rock in the intrusive mass. Nevertheless, the intimate sandwiching of innumerable veins or narrow sills of igneous material is undoubtedly an important feature of some synchronous bathyliths, where, indeed one may trace all gradations from igneous rock with linear inclusions of country-rock outwards into country-rock intimately seamed with igneous veins. The present writer, however, is inclined to regard these phenomena as being essentially marginal, either along the sides of the bathylith or at the top part where it frays out into an irregular roof, and not as being characteristic of the whole mass of the intrusion.

It is only in connexion with synchronous bathyliths that the author has observed true dykes of pagmatite, and especially the association of dykes of pegmatite and gabbro. Among the massive granite dykes of aplite, with or without complementary rocks, occur, but pegmatites appear mostly as segregation-veins. The conjunction of coarse acid and basic rocks cutting through the granite-gneiss, as at Broken Hill and Cooma, suggests a complementary relation.

Acid gneisses are found, though not extensively, along the margins of the granite-gneiss intrusions at both Broken Hill and Cooma, produced, it would appear, by dynamic differentiation like that described by Barrow for the granites of the South-Eastern Highlands[17].

An intrusion which is of the synchronous type, but which lacks some of the characters listed above, is the Upper Murrumbidgee bathylith, extending from Cooma northwards for about sixty miles into the Federal Capital Territory. Though it has not as yet been completely investigated, sufficient is known of its occurrence to permit of its main characters being determined, and a short description of it has been given elsewhere[9]. It differs from the intrusions already described in its association with slate as well as schist, in the complete absence of *lit-par-lit* injection and in the surprisingly small amount of contact-metamorphism associated with it. Also, though peripheral lenses of the intrusion are locally numerous and the intrusion frays out into a number of tapering tongues to the south, there is no shading-off or merging of intrusion into country-rock, and the boundary between invading and invaded rock is generally sharp. The main rock type is a quartz-mica-diorite grading into granite, but there is in places marked marginal development of very acid aplitic gneiss. Aluminous minerals produced by assimilation of

sediments are lacking, but well-crystallized primary epidote appears to be a constant constituent, in the marginal quartz-diorite at all events. It would appear that the conditions of heat and dynamic pressure attending this intrusion were less intense than in the other cases considered, and evidently the magma was less rich in volatile constituents.

A consideration of some of the characters of these intrusions enforces the conclusion that they were all injected after regional metamorphism had altered the sedimentary rocks, but while conditions of strong dynamic pressure still prevailed.

Notes on Subsequent Bathyliths.

The great majority of the known bathylithic intrusions in this State belong to the subsequent type, and the writer has tried elsewhere[9] to show that in the main these belong to two main epochs of intrusion, the one at the close of the Devonian Period and the other near the close of the Permian. But little has been done toward a systematic investigation of these intrusions, and it is doubtful whether the complete boundaries of any one bathylith have ever been traced. However, the general characteristics attributed to this type of intrusion, as listed above, have been determined as a result of the partial examination of a number of examples in this and other States.

Although it is true that massive granites are often found outcropping amid regionally-altered rocks, there are usually indications that these have received the metamorphic impress long before the date of the intrusion, and have really formed the floor for the geosynclinal sediments, now eroded away, which were folded just before the intrusion occurred. But it is probably the usual case that the granite has originally penetrated through the floor and

in among the just-folded sediments, and where these are found outcropping about the bathylith they may show little or no regional metamorphism, though contact-alteration may be marked.

It is apparently not uncommon to find in the subsequent bathyliths, in addition to the predominant granite or quartz-monzonite, minor amounts of more basic rocks such as granodiorite, diorite, gabbro, pyroxenite and hornblendite, and even peridotite, with intermediate connecting varieties. The consanguinity of these with the granite is clear on mineralogical and chemical grounds, and their field-relations may be such as to suggest a series of intrusions from some more deep-seated reservoir of differentiating magma. Examples are furnished by the Moruya[18] and Hartley[19] intrusions in this State and by the Meredith Range and other composite bathyliths in Tasmania.[20] In certain instances somewhat alkaline rocks may appear as final differentiates.[21, 22]

The very fact that this serial differentiation, whatever its mechanism, has been possible, points to the prolonged existence of tranquil conditions during the cooling of the magma. Moreover, the general absence of signs of regional metamorphism in the surrounding sediments, and of directive structures in the igneous rocks themselves, together with the cross-cutting relations of the intrusion, would indicate in the first place that conditions of compression had never been at any time very strongly marked, and, secondly, that compression had ceased and been replaced by tensional conditions at the time of injection of the igneous magma.

Depth-Variations in Habit and Structures of Bathyliths.

It may be argued that, just as the unaltered sedimentary rock may grade downwards into phyllite and schist as a

result of deep burial, so the massive transgressive granite of the subsequent bathylith may pass at depth into gneissic granite and granite-gneiss with the concordant habit of the synchronous intrusions—in other words that the differences in habit and appearance of the two types of intrusion as seen in outcrop are simply functions of depth of erosion. Barrell (*op. cit.* pp. 5 and 6) considered that different types of bathyliths owe their distinctive characteristics to the fact that "they may have approached to within a few thousand feet of the surface of the earth, into a zone of fracture and rapid cooling, or they may have ceased their upward progress at a depth of miles, while still in the zone of flow . . ."

Blackwelder and Baddley[23] apparently had something similar in mind when they wrote that "cross-cutting relation is characteristic of the more superficial parts of a bathylith and especially of those that approach nearer the surface, while at very great depth the marginal rocks become plastic and flow, making contorted gneisses."

In both these quotations there appears to be the implication that pressure and temperature are functions of depth, and depth below the surface is emphasized as the controlling factor in producing the distinctive features of synchronous and subsequent bathyliths. While this may be regarded as in a general way correct, there are certain phenomena which tend to show that the habit and internal structure of the bathyliths depend not on the existence of some actual limiting depth, but rather upon the conditions of temperature, and particularly pressure, existing at the time of injection and at the level of injection, conditions which may change from time to time. The most striking illustrations of this fact within the author's knowledge are to be seen in the neighbourhood of Broken Hill, where the masses of granite-gneiss with concordant habit are inter-

sected by small boss-like outcrops of perfectly massive fine-grained granite, exactly similar to the surrounding gneiss except for the total absence of directive structures, and beyond reasonable doubt derived from the same magma and injected during the same epoch of intrusion. It is a fair assumption that the load or depth of cover had not changed materially in the interval between the two sets of intrusions, and the conclusion is enforced that the differences in habit and internal structure are the result of change in the pressure-conditions, the horizontal or folding forces having died out and been replaced by tensional forces.

The change from compressional to tensional conditions after the consolidation of the main body of magma is also indicated by the existence of dykes of unstressed pegmatite, comagmatic with the granite, cutting across the primary gneissic foliation.

In this connexion a statement of Dr. Harker's has special significance. Commenting on Grubenmann's assumption that regional metamorphism is related simply to depth below the surface he remarks:[24] "We can conceive ideally a globe in which the temperature, like the pressure, increases steadily downwards; but it is of the essence of metamorphism that it is related to a very notable disturbance of this ordered state of things in some part of the earth's crust." In like manner the special characteristics of the synchronous bathylith, which is so closely associated with regional metamorphism, are not to be related simply to the normal change in temperature and pressure conditions with depth, but rather to the same special and transient conditions which have effected the metamorphism.

Nevertheless the habit of a plutonic intrusion, or its attitude towards the enclosing rocks, though not necessarily its internal structures, may be in some degree dependent on

depth, and may be found to undergo a change when traced downwards. In considering the results of horizontal compression of a portion of the earth's crust which has been the site of a geosyncline it is necessary to distinguish two elements which in general behave differently towards the compressive forces. The first of these elements consists of the recently-deposited sediments, now for the first time subjected to horizontal compression; these become folded and, perhaps, cleaved and metamorphosed, and overthrust along planes of low inclination. The second element is composed of the rocks which form the floor or basement of the geosyncline; these have probably been compressed and, it may be, strongly folded and metamorphosed during a much earlier period, so that from their attitude and condition they are now no longer capable of further folding, but act as more or less rigid masses which can yield only or mainly by thrusting along shear-planes. If the basement rocks are old igneous intrusions the same will happen. Lawson[25] and Daly[26, 27] are of the opinion that underthrusting is the most likely method of yielding, and the former considers that the gliding surface should be concave downwards, gently dipping above, but steepening rapidly below. It seems at least arguable that overthrusting would be just as likely to occur, in which case the curve of the gliding surface would be reversed, with the concavity upwards, a steep dip above shallowing rapidly almost to horizontality below; this would harmonize with Keith's[28] conception of the attitude of these rock-partings. However, the important point is that there would be differential thrusting movements of blocks or masses of the basement. The planes or zones of shearing, being very deep-seated, would naturally be very different from the flat overthrusts affecting the overlying folded sediments, and the intensity of the shearing would vary according to circumstances. The strikes of

the principal shear-zones would be more or less normal to the direction of horizontal pressure, and hence parallel to the axes of the folds produced in the overlying sediments, though not necessarily parallel to the strike of the basement-rocks, while there might be other minor transverse shear-zones. Reference to the shear-zones of the Barrier Ranges, which the author believes to have originated in this way, is made below.

Now when, either during or after folding, magma was forced upwards, its passage would be facilitated by the existence of the zones of weakness produced by the shearing and dislocation of the basement-rocks; its introduction at intervals along such shear-zones would therefore directly determine the general parallelism that so often exists between the arrangement of the bathyliths and the strike of the sediments among which they were injected. On the removal of these sediments by erosion, however, the bathylith would be seen to have no parallelism with the strike of the surrounding basement-rocks, except, of course, in the case where this happened to coincide with the axes of folding of the overlying sediments. Thus the orientation of an intrusion toward the country-rocks might be different in its upper and in its deeper parts.

What would appear to be an illustration of the foregoing principle is to be seen in the composite bathylith at Moruya, on the South Coast of New South Wales. According to Miss Ida A. Brown,[18] who has examined and mapped the area, the bathylith makes an elongated outcrop about three to four miles in width, which has been traced for twenty miles in a N.N.W. direction and extends much farther, the boundaries of the mass being sub-parallel. The invaded rocks, of early Palaeozoic age, are closely folded along a meridional direction, so that the bathylith cuts obliquely across the strike of the fold of these rocks. There are, as

Miss Brown shows, reasons for believing that the intrusion is of late-Devonian age, and, as a matter of fact, about six miles west of Moruya and not far from the granite boundary, gently-folded Devonian sedimentary rocks outcrop with a N.N.W. strike. The elongation of the bathylith, or of that part now remaining, is therefore parallel to the Devonian axis of folding, and it is the erosion of the roof rocks that has revealed the basement of older close-folded strata on which they were deposited. It is not unreasonable to suppose that the position and trend of the intrusion have been determined by a zone, or a series of zones, of dislocation developed through these basement rocks parallel to and contemporaneously with the folds in the overlying Upper Devonian strata.

Shape of Bathyliths.

It would appear from a consideration of the circumstances attending their injection, that the relations of synchronous and subsequent bathyliths towards the just-folded sediments will differ considerably, with a consequent difference in the shape of the upper parts of the intrusions. Where the folding of these geosynclinal sediments has been so intense as to produce sub-vertical cleavage and schistosity the synchronously-injected magma would tend to be forced up along these planes of relatively easy progress, and perhaps, by assimilation and replacement, might make way for itself so as to form sheet-like or phacoidal masses which would be relatively narrow, since there would be a direction of minimum ease of progress at right angles to the planes of weakness. But where the sediments had not been severely folded and regionally altered there might be a strong tendency for the magma, especially if severe horizontal compression had ceased, to spread out more or less laterally when it had reached the level of the base of the geosynclinal sediments, since the inducements to vertical

progress would then not be so great. This lateral progress might be primarily directed by the surface of unconformity, or by flat planes of overthrust developed in connexion with the folding of the sediments, but much vertical progress might be made along planes of jointing and dislocation, and by means of overhead stoping. Thus the subsequent bathyliths might really be of the nature of great floored intrusions, as imagined by Brøgger[29], Harker[30] and Iddings[31], and as inferred by Cloos from field-observations, whereas the synchronous bathyliths, elongated and concordant, might be of the shape that Daly conceives all bathyliths to have, with sides sloping steeply downwards, and extending without interruption or constriction to abyssal depths.

Bathyliths and Mountain-Building.

The association of bathyliths with regions and epochs of mountain-folding has often been stressed, and Daly has laid it down that "bathyliths are situated in a folded belt, and their date of intrusion has followed more or less closely an antecedent period of mountain-building." It would appear that in no case has a bathylith been found intrusive through flat-lying, unfolded sediments, and it is fairly safe to assume that there is a close relation between plutonic intrusion and crustal movements. But the differences between synchronous and subsequent bathyliths are very great, and it is necessary to explain these differences in terms of environment, or conditions prevailing during injection, while at the same time relating both types of intrusions to mountain-building movements.

It seems to be agreed at the present time by many students of mountain-building[32] that the formation of the great mountain-ranges of the world is not in general due to folding alone, but is the resultant of two main movements. First, there has been tangential compression and folding of geosynclinal sediments, which may or may not in

itself have resulted in considerable elevation of the sediments above sea-level. An interval of erosion seems to have succeeded, followed eventually by a movement of general vertical uplift; and it is this last which has accomplished most of the actual elevation of the mountain-range. The term *orogenic* has therefore lost its strictly etymological significance of *mountain-building* and must be employed simply to indicate folding. Though the folding and vertical movements may have been separated by a very long interval indeed measured in years, they are to be regarded as phases of the one mountain-building movement, and apparently in the past it has happened that the compressional and tensional movements and subsequent extensive denudation of the elevated region have all been completed in the interval between one geological period and the next, this interval being a diastrophic epoch.

It would appear not improbable that the distinctions between synchronous and subsequent bathyliths which may be attributed to environment are due to the fact that the former were injected during the first or compressive phase of the mountain-building movement and the latter during the second or tensional phase. If this view is correct the terms *synchronous* and *subsequent* should have reference to the contemporaneity or otherwise of the act of intrusion with the compressional phase, and not with the mountain-building movement as a whole.

Keith[28] has argued that mountain-folding results from synchronous igneous intrusion, and Barrell[3] that regional metamorphism is largely due to the same cause, but in the author's experience, certainly limited, there is clear evidence that considerable folding and regional metamorphism have been accomplished prior to the emplacement of the synchronous bathylith, and this agrees with the observations of others.[5]

In any case, on *a priori* grounds, the wonderful coincidence of the axes of synchronous intrusion with the strike of the folded beds is surely most reasonably to be explained as due to the folding forces having operated first, the magma being injected along the direction and in the positions thereby determined, and, besides, the orientation of inclusions, the gneissic banding, and above all the development of acid fringes on the leeward margins of synchronous bathyliths, indicate that the magma was the passive plaything of the orogenic forces rather than an active agent in producing them. But quite apart from all these considerations, cases have been recorded of moderate to intense folding and strong regional metamorphism unaccompanied by any deep-seated igneous intrusion whatever.

It would appear then that there are serious difficulties in the way of considering synchronous bathyliths as important factors in producing folding and the regional metamorphism which often accompanies it.

The case, however, is somewhat different when subsequent bathyliths are considered. If, as suggested above, there is some lateral spread of the magma at the upper levels along shear-planes or other surfaces of discontinuity, then the liquid magma under great pressure from below, and acting as a great hydraulic ram, may actually cause the broad gentle doming-up of the superincumbent strata on a regional scale, and so be an important, if secondary, factor in the second or uplift phase of the mountain-building movement.

It is not clear why plutonic injections should sometimes accompany folding and sometimes succeed it, nor why the intensely folded and altered sediments should have synchronous intrusions associated with them, while the moderately or gently folded and little altered sediments should be invaded only by subsequent intrusions.

An explanation may, however, be attempted on the basis of the theory of mountain-building advanced by Joly.[32] It seems legitimate to assume that the thicker the accumulation of sediments in the geosyncline the greater will be the intensity of folding and metamorphism suffered by the lower portions of them on the collapse of the geosyncline, both by reason of the depth of the zone of weakness in the earth's crust and because of the increased heat and pressure due to deep burial and the weight of superincumbent strata. The outcrops of highly folded and altered strata may therefore be looked upon as merely the remnants left by erosion of an originally very thick sedimentary series. Apparently thicknesses of as much as eight or ten miles of sediment have accumulated in some geosynclines before their final collapse.

Joly considers that the transgression of the ocean waters over the land follows on a sinking of the continental granitic layer of the earth in the basaltic substratum when this latter has been liquefied as a result of the storing-up of radioactive heat. The formation of a geosynclinal trough on the continental layer presumably necessitates local depression of the lower parts of this layer into the hot basaltic substratum, and the subsequent collapse of the trough and folding of the sediments involve by way of isostatic compensation a further depression of the granitic layer, with probable liquefaction. According to Joly "in the great vertical pressures from beneath, which act on such a protuberant mass, the mechanism which brings about intrusion of plutonic continental magmas into the heart of the mountain range finds direct and simple explanation." These vertical thrusts are induced especially during the regelation of the basaltic substratum, when also vertical elevation of the folded sediments is produced.

Now if the geosyncline be very deep the layer of granitic material underlying its floor may be thinned and weakened to such an extent that when folding of the sediments takes place the fused lower portions of the continental layer may be forced upwards through the shattered basement-rocks and among the folded sediments. Later when regelation of the basaltic layer causes the vertical phase of the mountain-building movement to occur, and the upper folded sediments are in a state of tension, the vertical pressure may force further magma upwards through them to form subsequent intrusions.

Where, however, there has been but little sagging of the crust, and a relatively shallow syncline has been formed, only moderate folding and little metamorphism will result from lateral pressure. The solid granitic layer will not be seriously thinned either through depression of the geosyncline or through isostatic compensation on its collapse, and so there will be no intrusions synchronising with the folding, only the granitic magma forced up by vertical pressure on regelation of the basaltic substratum appearing among the folded and elevated sediments.

Some Implications of Bathyliths.

The petrological study of bathyliths has received considerable attention, and there has been much speculation in regard to their mode of emplacement and their relations with the invaded rocks at depth, but it would appear that the historical or stratigraphical aspects of their occurrence have been, relatively speaking, neglected. Doubtless this is due in part to the difficulties, so frequently encountered, of placing the intrusions chronologically, no less than to the fact that the record of the history of the earth's crust is contained overwhelmingly, and is most clearly to be read, in the sedimentary rocks.

The importance of the igneous intrusions of pre-Cambrian times has been recognised in North America, because such a very large proportion of the pre-Cambrian terrain consists of plutonic intrusives that they cannot be ignored. The same state of affairs prevails in Western Australia, where the exposed formations are dominantly pre-Cambrian, the bulk of these consisting of granitic rocks, with minor amounts of altered sediments and lava-flows. Though the Palaeozoic and later granites in Australia do not bulk by any means so largely, still they are of very considerable total areal extent, and are deserving of stratigraphical study. An attempt to place the larger igneous intrusives of New South Wales in chronological order was made by the author[9] in 1929, and Professor E. W. Skeats[33] has recently outlined a suggested chronology for the Palaeozoic granites of Eastern Australia.

But apart from the petrological interests of our bathyliths and the intrinsic importance of the intrusive episodes of the geological story, the larger igneous intrusions may actually serve to throw light on geological events which are otherwise obscure, or whose direct record may have been utterly blotted out. Thus bathyliths may be of value not merely for what they are, but also for what they signify.

The association of bathyliths, whether synchronous or subsequent, with folded sediments is so widespread, and the probability of a genetic significance in this association is so great, that it is not too much to say, from what is known of their occurrence, that bathylithic injection takes place only during some stage of the diastrophism that closes a cycle of sedimentation, and that the magma is introduced under and through the just-folded sediments.

A logical corollary to this proposition would be that wherever a bathylith outcrops we may infer the former

presence, on or over that spot, of a series of geosynclinal sediments, terrestrial or marine, during whose folding and elevation the intrusion of the bathylith took place.

The consequences of granting this inference are important from more than one point of view.

Although it must inevitably happen that the geological age of many bathyliths cannot be determined with any degree of accuracy, still there are many instances in which a fairly exact age-determination may be made, for example through the finding of other outcrops of the same mass, whose relations to the associated sediments are such as to afford age-indications, or through the existence of mineralogical, chemical or structural peculiarities in the rock itself, which point to correlation with other intrusions of known geological age. Now if it is possible by any means to establish the geological age of an outcropping bathylith, then, even though the formation in connexion with whose folding and elevation it was injected has entirely disappeared through erosion, we may legitimately and confidently infer its former existence on the site of the bathylith. Thus the bathylith may have a certain stratigraphical and tectonic value, inasmuch as it supplies some information regarding former episodes of deposition and diastrophism, of which other and more direct evidence has been obliterated.

The stratigraphical implications of plutonic intrusions lead on to an obvious palaeogeographical one.

The palaeogeographer is concerned with determining and plotting the distribution of land and sea, of mountains and lowlands, of areas of erosion and areas of deposition, during different geological periods, and this he does very largely with the aid of geological maps showing the structures and present-day boundaries of the sedimentary formations.

Where, however, the deposits belonging to any one geological period have been removed by erosion over large areas, there may be difficulty in plotting accurately their original extent, and here the outcrops of bathyliths of known geological age may be of material service, inasmuch as they help to indicate sites of geosynclinal sedimentation, and of the resultant or subsequent folding, elevation and erosion.

Significance of Some Australian Intrusions.

Some of the foregoing statements will perhaps be better appreciated if a few actual examples be considered.

(*a*) *The Mundi Mundi Granites of the Barrier Ranges, N.S.W.*

In the Barrier Ranges around Broken Hill, shear-zones, some upwards of 200 yards in width, are developed in great perfection and in considerable abundance through the Willyama (Archaeozoic) Series; their distribution can be well studied on the maps accompanying Mr. Andrews' report. In places they cut across granite-gneisses, which are locally converted into cataclastic gneisses and into mica-schists; elsewhere garnet-sillimanite-gneisses involved in the shearing have suffered retrogressive metamorphism into mica- and sericite-schists, while gabbros pass into amphibole-schists. Both longitudinal and transverse shear-zones occur, the former being in some cases traceable into the latter, and the planes of schistosity are vertical or nearly so, while displacement of the affected formations is often marked where the shear-zone crosses the strike of the country. These shear-zones differ from ordinary overthrust planes in the width of the zone affected, in their approach to verticality and in the intensity of the shearing.

Since the metamorphosed Willyama strata and the granite-gneisses injected through them have been alike af-

fected it is evident that the shearing occurred after the epoch of folding and injection that closed the Willyama period of sedimentation.

To the south-west, west and north of Broken Hill, as at the Umberumberka Reservoir and at Poolamacca, the Willyama Series is invaded by massive as distinct from gneissic granites; these are the Mundi Mundi granites of Andrews. Mawson[34] has described similar granites from Boolcoomatta, across the border in South Australia, which he regards as the equivalents of these Mundi Mundi granites. These granites are clearly much younger than the granite-gneiss; and according to Andrews their positions of injection have been determined by the shear-zones noted above. Directly overlying the granites, and containing boulders of them, are the late-Proterozoic tillites of Poolamacca and Boolcoomatta.

In the Broken Hill Memoir it is argued that the shearing and folding of the Willyama Series are related, and that the Mundi Mundi granites are comagmatic with the Broken Hill granite-gneisses, having been injected during a later stage of the eruptive epoch that closed the Willyama sedimentation.

It is true that instances are known in which intrusions during the earlier part of a mountain-building epoch have been followed by others during the later part of the same epoch, when compressional forces have ceased to operate. But in the particular instance under consideration these later cognate intrusions are to be found, as pointed out above, in the shape of a number of boss-like outcrops of massive granite within the granite-gneiss, and some other interpretation must be sought for the Mundi Mundi and Poolamacca granites; that favoured by the writer is somewhat as follows:

At the close of the Willyama sedimentation metamorphism and folding took place, with the intrusion of the granite-gneisses and gabbros, and subsequently of the little bosses of massive granite during vertical uplift. A prolonged period of erosion was followed by subsidence and further sedimentation in Early Proterozoic times. This in its turn was ended by diastrophism, with folding of the sediments, shearing of the basement schists and gneisses, and injection of the Mundi Mundi and Boolcoomatta granites, largely along shear-zones, the main axis of intrusion being perhaps somewhat to the west of its position in closing Willyama times. The erosion that followed completely removed the Early Proterozoic sediments and cut well down into the basement rocks, revealing the shear-zones and laying bare the Early Proterozoic granite. In Late Proterozoic times occurred the deposition of the Poolamacca tillites and other rocks of the Torrowangee Series on top of the outcropping granites and schists.

Thus, if the principle be accepted that abyssal injection implies precedent geosynclinal sedimentation and diastrophism, we can infer from the presence of these massive granites the deposition and folding of an Early Proterozoic sedimentary series, of which no traces remain upon the present surface.

(*b*) *The post-Silurian Granites of Tasmania.*

These, with their attendant basic and ultra-basic rocks, are by far the most extensive, and important economically, of the plutonic intrusions in the island-State. They were formerly referred to as the Devonian granites, for what reason it is not quite clear, but possibly because of a supposed correlation with the Victorian granites and granodiorites, which were tentatively regarded as early-Devonian. If the correlation stands, then in view of recent discoveries

as to the age of the Victorian rocks[35] the Tasmanian granites should now be considered to be late-Devonian. But in 1921 Hills[36] gave it as his opinion that they were epi-Silurian, and the question arises as to which view is correct.

If it be agreed that granite bathyliths are always injected under and through just-folded geosynclinal sediments, then, since no Devonian strata whatever are known to outcrop in Tasmania, it would be unsound to argue for a late-Devonian age for these granites, unless indeed magmatic peculiarities are sufficiently marked to warrant definite correlation with the late-Devonian intrusions of the mainland. Unfortunately the petrology of the Tasmanian granites has not been worked out sufficiently to permit of detailed comparison, and in the circumstances it is most natural and logical to assign tentatively to these rocks a late-Silurian age, inasmuch as the youngest strata into which the granites are intrusive are the folded Silurian. If at some future date comparative petrology can establish consanguinity between these rocks and the late-Devonian intrusions of Victoria and New South Wales, then a strong case will have been made out for the former extension of the Devonian sea to Tasmania, though all its deposits have since disappeared.

(*c*) *The Permo-Carboniferous Granites of Eastern Australia.*

There is another rather interesting and important palaeogeographical problem on which some light may be shed by a consideration of the distribution of bathyliths, namely the former extent of the area of deposition of Permo-Carboniferous strata in this State. At the present day the principal area where these strata outcrop is that forming what is called by the State Geological Survey the Main Coal Province, a broad belt extending in a N.N.W.-S.S.E. direction for over 200 miles, and stretching along the coast from Newcastle to the Clyde River. Scattered but considerable

outcrops occur in the north and north-west of the New England plateau, as about Drake and Ashford, and another occurrence centres round Kempsey in the south-east of New England; everywhere the strata are to a greater or less extent folded. The New England plateau is composed largely of ancient, more or less metamorphosed sediments, possibly in part Ordovician, broken through by bathyliths of granitic rocks which have been shown[37] to be in places intrusive through strata of Permo-Carboniferous age. The main outcrops of plutonic rock are found in the western and central parts of the plateau, and have been traced as far south as Tamworth and Nundle, and even to the Barrington plateau; scattered outcrops also occur to the east, extending over to the coast. To the north the granites continue across the border into Queensland, where they invade the Permo-Carboniferous beds to the south of Warwick.

It has been assumed by some authorities that the present eastern and western boundaries of the Main Coal Province (which are roughly parallel) coincide approximately with the original limits of a Permo-Carboniferous geosyncline, which was bounded to the east by highlands, composed of old rocks, separating it from an eastern area of deposition. Such a conception appears very definitely in the writings of Sir Edgeworth David[38] and E. C. Andrews.[39] A. B. Walkom[40] in discussing the matter likewise considers an area roughly north from Nundle to Inverell and eastwards to Hillgrove to have been land throughout Permo-Carboniferous times; the present surface-rocks of this area are mostly granites and old slaty rocks. Benson,[41] however, in 1923 published a palaeogeographical map showing the whole area between the Main Coal Province and the present coastline as a site of Permo-Carboniferous deposition, but without discussing the palaeogeography in detail. Bryan[42], in 1926, tacitly adopted Benson's views.

It is clear, therefore, that there is no unanimity in regard to the distribution of Permo-Carboniferous land and sea in New South Wales.

Now the Main Coal Province is bounded on its eastern side by Mesozoic or Early Tertiary faults which have raised the older rocks to the east by more than 5000 feet in places as compared with the Permo-Carboniferous strata, and it is, therefore, at least probable that these latter originally extended much further to the east that at present, especially as there are quite considerable thicknesses of strata still showing right up to the fault-planes. Erosion following quickly on the faulting would account for the present absence of the younger rocks on the eastern or upthrow side.

But quite apart from this, if we are to accept the evidence of the granites, then, since they are mainly late Permo-Carboniferous in age, it is necessary to postulate an area of deposition once extending well over to the east of the Main Coal Province, and a study of the geological map suggests strongly that Permo-Carboniferous sediments, freshwater or marine or both, once completely covered what are now the northern and central parts of the New England Plateau, perhaps as far east as the coast, and that on the south they extended continuously across from the Main Coal Province to Kempsey, even as Benson has indicated. In Queensland, according to the map accompanying Skeats' paper[33], the Permo-Carboniferous granites extend northwards along a broad coastal strip to within 120 miles of Cape York. It would follow, if this is correct, that both Benson and Bryan in their palaeogeographical maps might have extended the site of the Permo-Carboniferous sedimentation northward almost to the most northerly point of Queensland.

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THE AMOUNT OF HYDROCYANIC ACID IN SORGHUM, SUDAN GRASS AND SOME HYBRIDS.

By H. FINNEMORE, B.Sc., F.I.C.,

and

C. B. COX, B.Sc.

(Read before the Royal Society of New South Wales, Sept. 2, 1931.)

The object of the experiments detailed in the present paper was twofold, firstly, to ascertain the variation in the amount of hydrocyanic acid exhibited by different varieties of sorghum, and secondly, to determine to what extent it might be possible, by crossing sorghum with sudan grass, to breed hybrids containing a smaller amount of hydrocyanic acid, and thus reduce the danger to stock that is now incurred when fed on this valuable fodder. Although the original programme has been curtailed by the cessation of financial assistance to the Poison Plants Committee by the Council of Scientific and Industrial Research, it is the intention of this Committee to continue these experiments during the coming season.

It is now about thirty years since Dunstan and Henry[1] showed that when sorghum was cut or bruised, contact was made by the enzyme and the glucoside, with the result that hydrocyanic acid was immediately evolved. They also succeeded in isolating the glucoside which they termed dhurrin from the native Egyptian name of the plant, and showed that in addition to hydrocyanic acid, it gave on decomposition, 1.4 hydroxybenzaldehyde and glucose. These

observations were accompanied by the equally valuable one that the production of hydrocyanic acid increases with the development of the plant and then rapidly diminishes. Such questions then arose whether all varieties were equally toxic and whether the plant could be rendered innocuous by drying or by other means. One of the early workers on these problems was J. C. Brunnich, of Brisbane, who in 1903[2] made an investigation of two varieties of sorghum, viz., Planter's Friend or Imphee and Early Amber, and found the amount of hydrocyanic acid varied in the fresh plant from 0.027 to 0.035 and 0.011 to 0.014 per cent. respectively for the two varieties named, the higher figure in each case being obtained from the manured plant, at the same time confirming the decrease in hydrocyanic acid as the plant developed.

In 1912, Schroder and Dammann[3], working at Monte Video, examined three varieties of sorghum grown in Uruguay, and found the following amounts—from the variety *saccharatum*, 0.030; *vulgare*, 0.020 and from *halapense*, 0.014 from 100 grammes of the fresh plant. These quantities decreased as the plant matured, but the acid did not disappear entirely; there was an increase of 33 to 100 per cent. in manured plants.

Two American investigators, Willaman and West[4], in 1915, examined a number of sorghum plants and obtained a maximum of 83 milligrams per 100 grammes, calculated on a dry weight basis of the whole plant, which at that time was 18 inches high. After 62 days the plants had attained a height of 61 inches and then contained a neglible amount of hydrocyanic acid. In the following year[5] they maximum of 114 milligrams when the plant was 14 inches high, whilst there was only a trace when the height had increased to 78 inches after 92 days growth. A few years

carried out a similar series of experiments and found a later, Dowell[6], working at Oklahoma Agricultural Station, found one sorghum of 32 inches growth gave 22.2 milligrams and 22.8 milligrams (second growth), calculated on the fresh plant. Menaul and Dowell[7] obtained from fresh sudan grass 15 inches high, 10.5 milligrams, equivalent to 57.9 milligrams on the dry weight, the amount becoming less on later growth. In 1919, Colleson[8] working in Florida, examined twenty-one varieties of sorghum and found that they contained from 0 to 3.8 milligrams of acid, Dwarf Hegari and Feterita being the varieties containing the largest amount. Swanson at Kansas Agricultural College in 1921[9], reported "large amounts" of hydrocyanic acid in sudan grass, and later[10] determined the amount present under various conditions. Practically the whole of the acid was yielded by the leaves and the maximum was found to be from a whole plant 4 inches high, this being 20 milligrams. There was a loss on drying, but the acid did not entirely disappear after wilting for 5 days. This plant gave less acid than sorghum or kafir. In 1923, Brunnich[11] reported on the various sorghums at different stages of growth. There was much variation in the hydrocyanic acid at three weeks and later cuttings showed greatly reduced amounts.

Recently the analyses of nine hybrids have been published by Ramsay[12], these were bred from Saccaline sorghum as the male and sudan grass as the female. Some plants were examined when 4 feet high, but most of them were 12 to 18 inches high. The amount of acid varied from nil to 11 milligrams per 100 grammes, the largest amount being obtained from a 4 feet hybrid. Pure sudan grass, height not stated, gave only 0.01 milligrams and pure saccaline, 3 milligrams. In this connexion it should be

noted that as neither the method of analysis nor the condition of the material was stated the results obtained emphasize the importance of further investigations.

Experimental.

The plants used in these experiments were sown at the Glenfield Veterinary Research Station on October 15th, 1928. For the necessary arrangements the authors are indebted to the Director, Dr. Seddon, who has kindly supplied the following particulars. Altogether, 18 sowings in numbered rows were made. These consisted of eight sorghum-sudan grass hybrids, varieties of sorghum and one row of sudan grass. The seeds of 6 hybrids had been obtained in 1926 from Mr. A. N. Whittet, N.S.W. Government Agrostologist, those numbered 1 and 6 in the Table, had been grown on unbagged heads, whilst Nos. 2 to 5, inclusive, were from bagged heads. The remaining two hybrids had been obtained from the same source in the month previous to sowing.

The determinations of hydrocyanic acid were made at various stages of growth, the age of the plant in days being shown in the table. Before carrying out quantitative measurements each sample was tested qualitatively by cutting up about 1 gramme finely with scissors and macerating in water in a closed test tube, the colour imparted to a sodium picrate paper being taken as an indication of the presence of hydrocyanic acid, which was then determined, some of the qualitative tests being carried out at Glenfield within half an hour after gathering the specimens.

Method of Estimation.

It seems more than probable that some of the results quoted above are not strictly comparable, for, in some cases, there is no information as to the moisture in the material

examined, nor of the method employed, so although the results of each worker may be consistent in themselves, they cannot necessarily be compared with those of other workers. Such factors as the possibly incomplete hydrolysis of the glucoside, the difficulty in removing the hydrocyanic acid when formed, and the possible existence of various combinations of hydrocyanic acid with other constituents of plants have all been shown to be important factors in this connexion. Swanson showed that the maximum yield was obtained from sorghum by macerating for 6 hours or overnight at room temperature, and this procedure was adopted. Several whole plants, exclusive of roots, were passed through a meat mincer in order to obtain a thoroughly representative sample. Twenty grammes of this were macerated in a tightly closed flask with 300 cc. of distilled water overnight at room temperature. The contents of the flask were then distilled in steam until all the hydrocyanic acid had been removed, the distillate being collected in an excess of decinormal sodium hydroxide. This was then made acid with hydrochloric acid and titrated with decinormal iodine in the presence of sodium bicarbonate. Under these conditions 1.4 hydroxybenzaldehyde which is also a product of the reaction was found to be non-volatile in steam and therefore did not affect the result.

Parallel with the estimation, when sufficient of the sample was available, the moisture lost on air drying was recorded,* twenty grammes of the disintegrated material being set aside until the weight was constant. The time required for this varied from eight to fourteen days.

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* In later experiments with other plants it has been found preferable to dry at 100° to constant weight and in further work on sorghum this modification will be made.

The Amount of Hydrocyanic Acid in Sorghum and Allied Plants from Seed Sown at Glenfield V. R. S. on 15/10/'28.

	Number of Milligrams of HCN in 100 grams of—									
	Fresh Plant.				Air-dried Plant (calculated).				Air-dried Plant (found)	
Age of Plant in days ...	42	64	90	97	42	64	90	97	42	64
Size in inches	6-12	20	60	60	6-12	20	60	60	6-12	20
Name, Row and No.										
Sorghum sudan hybrid—										
1 I	—	21	—	18	—	99	—	43	—	41
do. 1 2	—	27	5	17	—	157	19	44	—	98
do. 1 3	37	22	13	20	181	116	44	78	129	43
do. 1 4	—	18	14	16	--	81	75	62	—	44
do. 1 5	—	—	—	—	—	—	—	—	—	—
do. 1 6	—	21	15	12	—	98	47	34	—	55
do. 2 7	2	7	5	5	12	34	15	14	10	12
do. 2 8	--	13	8	10	—	58	20	28	—	28
Saccaline 3 and 4... ..	36	11	4	8	172	57	23	30	121	48
Collier 5 and 6	54	19	2	6	262	101	14	26	153	52
White African 7 and 8 ...	53	45	6	6	282	223	29	40	160	—
Sumac 9	44	35	11	14	243	160	37	42	140	54
Cowper 10 and 11 ..	36	25	12	8	192	129	53	39	144	62
Sudan Grass 12 and 13 ...	9	12	4	3	—	43	13	10	—	35
Number 34 14 ...	33	31	4	9	145	169	12	39	112	52
Feterita 15 and 16 ...	111	75	20	23	—	331	67	73	—	138
Milo 17 and 18	50	33	8	19	248	163	25	73	135	57
Gooseneck 19	—	69	8	19	—	291	32	72	—	137

All the above were free from HCN 132 days after sowing.

From the percentage of moisture and of the hydrocyanic acid yielded by the fresh plant, the amount obtainable from the dry material was calculated. Of the specimens collected in November and December actual determinations of the hydrocyanic acid in the dry plant were made, but in the samples gathered later this was so small that its amount was not considered of sufficient interest. The results are set out in the table.

Conclusions.

1. All the varieties examined yielded some hydrocyanic acid up to about 130 days after sowing, when the seeding stage had been passed, but the amounts varied considerably. Some gave larger percentages than have hitherto been recorded, sudan grass gave the least and feterita the most.

2. Owing to slow germination only two of the eight hybrids were available at the time of the first examination, but from the second series of results it seems that these hybrids are lower in hydrocyanic acid, at all events, in the first month or two, than the majority of the sorghums.

3. The results of other workers have been confirmed in that the percentage of hydrocyanic acid has been found to be greatest in young plants and to diminish as growth proceeds.

4. Under the conditions specified the loss of hydrocyanic acid on exposure to the air, varied from 14 to 65 per cent. These two particular specimens still contained when air dry, 48 and 54 milligrammes of hydrocyanic acid per 100 grammes, and reference to the table will show that other specimens yielded higher results than these. As Seddon and King[13] have shown that, in the presence of sufficient enzyme, as is the case with the sorghums examined, a quantity of 50 milligrammes, per 100 grammes in the dry plant is likely to render it toxic, it would appear that young

sorghum, even when wilted, cannot always be considered safe as fodder.

It is desired to acknowledge a grant from the Council of Scientific and Industrial Research to the Poison Plants Committee, that has enabled one of us (C.B.C.) to participate in this work.

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A CONTRIBUTION TO THE CHEMISTRY OF THE FRUIT OBTAINED FROM THE WHITE CEDAR TREE (*Melia Azedarach, L.* var. *australasica* C.DC.; Syn. *Melia australasica,* A. Juss.) GROWING IN NEW SOUTH WALES, WITH NOTES ON ITS REPUTED TOXICITY.*

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(Read before the Royal Society of New South Wales, Sept. 2, 1931.)

The information recorded in this paper embraces the results of an investigation undertaken in 1922, for the purpose of ascertaining the chemical composition of the fruit obtained from the White Cedar Tree growing in New South Wales. At the same time, in view of the fact that cases of apparent poisoning had previously been observed and recorded in both human beings and animals after eating the fruit, it was realised that the isolation and identification of the supposed toxic constituent was an urgent necessity. This fact was emphasised during the progress of the work by reports of additional cases of poisoning having occurred at that time, and indicated the necessity for concentration for the time being on that particular portion of the investigation. Curtailment of the original work undertaken naturally followed, and later, owing to pressure of official work, it was found impracticable to complete the investigation, both in regard to the chemical composition of the fruit, and identification of the toxic constituent, as was

* Toxicity tests conducted by R. GRANT, F.C.S., formerly Assistant Microbiologist, Department of Public Health, Sydney.

originally intended. The matter has been held in abeyance since 1927, but, owing to numerous enquiries recently received by the Institution regarding the toxicity of the fruit, and in order that later workers in the same field of investigation might become acquainted with what had already been done, it was considered advisable to publish, without further delay, the results obtained.

In order to facilitate the isolation of the toxic principle of those fruits which were reputed to be poisonous, Mr. R. Grant, F.C.S., then Assistant Microbiologist of the Department of Public Health, Sydney, through the courtesy of the Director General of Public Health, kindly undertook feeding experiments on guinea pigs, utilising the several portions constituting the fruit, e.g., meal, skin, seeds, etc., in addition to extracts prepared therefrom. As a result of these practical tests it was hoped that the particular portion of the fruit containing the toxic principle would be speedily indicated.

A large number of feeding tests was conducted over a period of about five years, with varying, and often disappointing, results. The fact, however, appears to be established that, when present, the toxic constituent occurs in the resinous portion of the fruit, and further, that a substance of alkaloidal nature exists in the resin. Evidence was also obtained that, whereas neither the alkaloidal portion of the resin, nor the resin from which the former was extracted, proved toxic when administered alone, a mixture of both produced fatal results.

It was found, however, that, whilst fruit obtained from trees growing in certain localities (Parramatta and Dubbo) contained the toxic principle, that obtained from trees growing in another locality (Grafton) proved harmless when eaten, and this variation was at first thought to be

due to seasonal changes, soil conditions, or other causes; according to information kindly furnished by Mr. E. Cheel, Curator of the National Herbarium, Botanic Gardens, Sydney, however, the occurrence of at least two forms of the species might readily account for the varying results obtained.

Analogous cases are to be found in Australian essential oil yielding species; the occurrence of varieties of a particular species, all botanically identical, but differing in the chemical composition of the oil present in the leaves, has been brought to light during recent researches carried out at this Institution. (Proc. Royal Society of New South Wales, 1922, Vol. 55, pp. 82-87; 1927, Vol. 61, pp. 54-67; 1930, Vol. 64, pp. 264-297.)

With regard to the White Cedar, the following extract from a letter written by Dr. John MacPherson, of Sydney, is of special interest:—

"My friends in the country inform me that the domestic fowls and turkeys eat up all the fallen 'berries' with avidity without sustaining any harm. But they noticed a curious thing, namely, that of three trees together, all bearing profusely, the Black Magpies stripped one tree bare and never touched the fruit of the others."

As set forth under "Experimental," fruit from trees growing at Grafton, Dubbo, and Parramatta respectively, in New South Wales, were examined, and later, a parcel of fruit from trees growing at Richmond, New South Wales, was also tested for toxicity.

Previous Observations Regarding Toxic Properties of White Cedar Fruit.

The late Mr. J. H. Maiden in "Forest Flora of New South Wales," Vol. 3 p. 93, cites a number of cases of poisoning having followed the eating of White Cedar Fruit by both humans and animals; pigs appeared to be par-

ticularly susceptible, and a number of fatal results followed the eating of the fruit.

An examination of fruit for the presence of hydrocyanic acid was carried out by F. B. Guthrie (Agricultural Gazette of New South Wales, 1897, p. 700) but none was detected.

Description of Tree.

The species *Melia Azedarach L.* Var. *australasica* C.DC. (Monogr. Phan. i 1878, 452); Syn. *Melia australasica*, A. Juss, is described by Bentham in "Flora Australiensis" (Vol. 1, 380), and is also figured and described by J. H. Maiden in "Forest Flora of New South Wales," Vol. 3, p. 93. The tree is stated to reach a height of 40-60 feet, and "its habitat extends from a little north of Sydney along the coast and coastal districts to North Australia." The tree responds readily to cultivation, and some of the fruit used in the present investigation was obtained from cultivated trees.

Description of Fruit.

The ripe berry or drupe consists of a hard, ribbed seed (the ribs varying in number from four to seven) surrounded by a pasty, sticky pulp, the whole being enclosed in a rather tough, golden-yellow skin. The odour is "sharp" and characteristic. The taste is at first sweet, but immediately afterwards becomes decidedly bitter. Prior to ripening, the firm, green berry contains a milky emulsion. Those obtained from trees growing at Grafton, New South Wales, were ovoid in shape, whilst the berries from trees growing at both Dubbo and Parramatta in the same State, were more spherical or globose than the Grafton berries. One hundred ripe berries chosen at random from the Grafton consignment weighed 67 grams, equivalent to an average mass of 0.67 gram. The dimensions of the smallest berries averaged 12 mm. long by 8 mm. short diameter, and mass

0.3 gram; the largest averaged 18 mm. by 11mm. and mass 1.07 gram;; whilst the medium sized berries averaged 16 mm. by 11 mm. and mass 0.7 gram.

Composition of the Fruit.

The results of the chemical analysis of the ripe fruit, show that the principal portion, i.e., the pulp, comprises a meal consisting largely of starch, an oil, a resin, and a reducing sugar, identified as dextrose. Water-soluble substances of acid nature are also present. The hard seed contains a number of small kernals which yield a fixed oil. A tough skin encloses the fruit.

The moisture content of ripe berries from various parcels received, varied from 18% to 29%.

Experimental.

The majority of the work to determine the chemical composition of the ripe fruit was performed on a parcel of fruit obtained in July, 1922, from trees growing at Grafton, New South Wales, which parcel was kindly supplied by Mr. Eugene Rudder. This gentleman has devoted much time and energy to the utilisation of White Cedar berries, and acknowledgment of his efforts is gladly recorded.

The abovementioned parcel of fruit, after removal from the stalks, weighed 15¼ lbs.

Extraction of fruit by Solvents.—The skin of each berry was broken in order to facilitate extraction of soluble matter by solvents, and the fruit placed in a vessel, and covered with cold ethyl ether; after standing for three weeks, the ethereal solution was poured off, the fruits washed with a small quantity of fresh ether (which was added to the ethereal solution), and the fruit allowed to stand in contact with cold 95% alcohol for two months. The alcoholic solution was then removed, and after washing with the same solvent, the fruit was treated with boiling water, which

treatment separated the insoluble portion of the pulp (meal) from the seed, and also dissolved the remaining soluble constituents of the pulp. The meal was separated by filtration, washed with water and dried. Separation of the skins from the seeds was effected by rubbing the fruit between the palms of the hands under water, whereby the seeds sank to the bottom of the vessel and were collected, whilst the skins were suspended throughout the liquid, and were recovered by filtration.

Proximate analysis of Grafton fruits.—As a result of the previously described treatment, the following approximate percentage composition of the Grafton fruit was obtained :—

	Per cent.
Ethyl ether-soluable extract	3
Alcohol-soluble extract	7
Water-soluble extract	20
Meal	4
Skin	5
Seeds	41
Moisture in original fruit	20
	100

For purposes of comparison, and in order to show the variation in composition, the proximate analysis of a parcel of fruit obtained in June, 1923, from trees growing at Dubbo, New South Wales, is appended :—

	Per cent.
Petroleum-ether extract	0.2
Ethyl ether-extract	0.6
Chloroform-extract	0.7
Alcohol-extract	7.0
Water-extract	18.3
Meal	4.0
Skin	4.7
Seeds	46.5
Moisture in original fruit	18.0
	100.0

Note.—The above analysis was carried out by extracting fifty berries, weighing 42 grams, in a Soxhlet apparatus with the first four solvents successively; the water soluble portion was obtained by agitating the berries from the above treatment with cold distilled water until all soluble matter had been removed. The meal, skins and seeds were recovered as previously described in the treatment of the Grafton berries.

Ether Extract of Grafton fruit.—The ethereal solution from 15¼ lbs. of fruit was concentrated to small bulk by distillation of the solvent, and at this stage a small quantity of white nodules separated from the concentrated solution; these were removed by filtration, and washed with cold ether. The concentrated ether solution was poured into a shallow dish, and the last traces of ether removed by gentle heat. On cooling, a turbid, yellowish, resinous mass remained which possessed the characteristic odour of the ripe fruit. The weight of the material was 213 grams.

White nodules separated from concentrated ethereal extract of fruits.—The white nodules were crushed and recrystallised from boiling ether in which they were sparingly soluble. The crystalline material melted at 192-205° C. in an open capillary tube, and at 205-210° in sealed capillary tube (in sulphuric acid bath). The substance did not reduce Fehling's solution, and when boiled for some time with weak sulphuric acid, and again tested with Fehling's solution, a negative result was obtained. It does not appear, therefore, to possess glucosidal properties.

Resolution of ether extract into Fat and Resin.—A portion of the ether extract (111 grams) was triturated with two successive portions of petroleum ether (b.pt. 32-50° C.), until all soluble material had been extracted; the solution was filtered, and on removal of the solvent,

59 grams of clear, pale-yellow viscous oil were obtained.

The insoluble material consisted of 49 grams of brittle resin, which was readily crushed to a light-yellow powder.

Analysis of oil.—The oil possessed a "resinous" odour, and after standing for some time, became turbid; it also possessed a slight "tackiness" when tested between the finger, thus indicating the presence of resin. Portion of the oil (48 grams) was agitated with two successive portions of 100 c.c. alcohol, which solvent dissolved the resin, and after separation of the alcoholic solution, 32 grams of clear, viscous oil were recovered which possessed a slight odour and bland taste.

On removal of the alcohol from the separated solution, 14 grams of a clear, tacky resinous mass were obtained, which apparently contained a proportion of the oil in admixture. The following physical and chemical characteristics are those of the oil before, and after, treatment with alcohol:—

	Before (49 grams).	After (32 grams).
$d\frac{15^{\circ}}{15}$	0.9735	0.9523
n_{D}^{20}	1.4930	1.4845
Acid Value	9.1	3.4
Saponification Value	150.6	164.9
Iodine Value (Wijs, 2 hours)	145.05	150.7

Mixed fatty acids.—A portion (21.3 grams) of the 32 grams of oil was saponified with alcoholic KOH and the resulting soap agitated with ether; 3.6 grams of unsaponifiable material were obtained which were again treated with alcoholic KOH, and the unsaponifiable material removed by ether; 2.95 grams of a light-yellow, clear, resinous mass were obtained, thus indicating that portion of the resin had remained in the oil.

The soap solution was decomposed with dilute sulphuric acid and the liberated fatty acids washed with hot water until free from mineral acid. On cooling, 15 grams of a semi-solid crystalline mass of mixed fatty acids were obtained, which retained a resinous odour and slight "tackiness."

Determination of Resin acids in mixed Fatty acids.—The method of Twitchell described by Dieterich in "Analysis of Resins" (1930, p. 49) was employed, with the following result:—

0.6774 gram mixed acids gave 0.1040 gram resin acids $= 15.35\%$ resin acids.

It is thus apparent that the oil still contained a considerable proportion of resin.

Separation of "liquid" and "solid" fatty acids.—The mixed fatty acids were resolved into "liquid" and "solid" acids by the lead salt-ether method. The following constants were obtained for the respective acids:—

"Liquid" acids.	"Solid" acids.
Neutralisation value, 132.4	Melting point, 55° C.
Mean molecular weight, 314.	Mean molecular weight, 274.
Iodine value (Wijs, 2 hrs.) 119.4	

Bromides of "liquid" acids.—A portion (5.6 grams) was dissolved in 50 c.c. dry ether, the solution cooled to —20° C., and saturated with bromine; after 24 hours a minute quantity of precipitate was observed, but this was too small to handle. The ether was allowed to evaporate, and the pasty mass triturated with light petroleum ether at —20° C.; very little appeared to dissolve, and the solution was decanted from the insoluble resinous portion. A clear, viscous, light-yellow liquid was recovered from the petroleum ether solution after allowing the solvent to evaporate. The proportion of bromide present was deter-

mined by boiling with concentrated nitric acid and solid silver nitrate.

0.3796 gram liquid bromide gave 0.3384 gram AgBr. = 37.93% Br. The bromide of oleic acid contains 36.18% of bromine.

Elaidin test.—Portion of the original liquid acid, which possessed an odour of oleic acid, yielded a pasty, orange coloured mass when treated with sodium nitrite and nitric acid.

The liquid fatty acid apparently consists of oleic acid.

"Solid" acids.—Efforts to resolve the crystalline "solid" acids into their separate constituents were not successful, owing to the small quantity available. A consideration of the melting point, and mean molecular weight, however, indicates that they consist of a mixture of palmitic and stearic acids.

Resin from ether extract.—The light yellow, brittle resin, after crushing to a fine powder, and thoroughly drying in the desiccator, possessed a characteristic odour, and gave the following figures on analysis:—

Melting point (taken on cover glass over mercury) 102°C.
" " in capillary (in sulphuric acid bath) agglutinated at 80°C, melted completely at 100-105°C.

Specific Gravity of fused resin	1.1533
Acid value	17.7
Saponification value	155.82
Iodine value (Wijs, 2 hours)	117.6 (approx.)

The resin fused to a clear, yellow viscous liquid on the water bath, and, on cooling, formed a clear, golden-yellow, glassy mass. Its solubility in various solvents was determined approximately, with the following results:—

Hot or cold petroleum ether (b.p. 32-50°).	Almost insoluble.
Absolute alcohol	Soluble.
95% alcohol	Soluble.
Chloroform	Soluble.
Ethyl ether	Soluble.

Benzol	Moderately soluble.
Hot or cold turpentine ..	Very sparingly soluble.
Amyl alcohol	Soluble.

Treatment of a fragment of the resin with concentrated sulphuric acid gave a dark red colour, changing to a dark brown. A solution of the resin in alcohol gave, with ferric chloride, a greenish colouration.

Saponification of resin.—Ten (10) grams were saponified by boiling with 3 grams potassium hydroxide in 60 c.c. alcohol for one and a half hours, the solution poured into water, and the watery solution extracted with ether; on removal of the ether from the extract, 3.3 grams of a light yellow, brittle resin were recovered. It was redissolved in ethyl ether, and petroleum ether (32-50°C) added until the solution became faintly turbid, and set aside for two days, when the solvent evaporated and crystals appeared throughout the resinous mass. Efforts to recover the crystalline material were not successful.

The aqueous solution was concentrated to small volume on the water-bath, and decomposed with dilute sulphuric acid, the resin acids separating as a brown viscous mass; it was washed with hot water until free from mineral acid, and dried; 4.2 grams of dark brown, "tacky" acid being obtained. It gave a neutralisation equivalent of 102.1.

The aqueous liquid from which the resin acids had been separated was neutralised with potassium hydroxide, concentrated to small volume on the water bath, and extracted with ether. The ethereal solution was separated, and the solvent removed; 0.0254 gram of viscous, brownish coloured material, possessing a phenolic odour was thus obtained. Its solution in alcohol gave a dark red colour with concentrated sulphuric acid, but ferric chloride produced no colouration.

No further work was carried out on the resin.

Alcoholic extract of fruit (after ether treatment).—The alcohol was removed from the solution by distillation under reduced pressure, and the resulting product was a dark, reddish-brown solution in water (originally present in the fruit). It possessed a sweet, followed by a bitter, taste, and was decidedly acid in reaction. The solution was agitated successively with petroleum ether, ethyl ether, and chloroform, but traces only of resinous bodies were extracted. Treatment with basic lead acetate solution gave a yellow precipitate, which was filtered off, washed, suspended in water, and decomposed with sulphuretted hydrogen. The resulting filtrate from the lead sulphide was tested for organic acids, etc., but no definite result was obtained.

The filtrate from the original lead acetate precipitate, was treated with sulphuretted hydrogen to remove any lead salt present, and concentrated to a thin syrup under reduced pressure. On warming a small quantity of the syrup with sodium hydroxide, ammonia was freely evolved. The syrup possessed a sweet taste, and gave a flocculent, almost white precipitate, with phosphotungstic acid in the presence of sulphuric acid. No definite result was obtained on examination of this precipitate.

Osazone.—Portion of the solution was taken and an osazone prepared in the usual manner; the derivative was recrystallised from 50% alcohol, and the characteristic crystals melted at 206°. The reducing sugar, dextrose, is, therefore, present.

Fehling's solution was readily reduced by the syrup.

In order to determine if the sugar was originally present in the fruit as dextrose, a few of the fresh ripe berries were placed in distilled water for a few hours; the aqueous solution was filtered and portion tested with Fehling's solu-

tion when a marked reduction of the copper sulphate solution occurred. An osazone was prepared from a portion of the aqueous solution, and, after, recrystallisation, melted at 206°C.

Water extract of Fruit (after alcohol treatment).—The fact that boiling water was used principally for the purpose of obtaining the meal, skin and seeds in a clean condition, militated against the examination of this extract owing to changes which would probably occur at that temperature. The solution was treated with basic lead acetate, but nothing definite was obtained from the precipitate thrown down. An osazone was prepared from the filtrate after freeing from sulphuretted hydrogen, and, after recrystallisation, melted at 207°C. (osazone of dextrose).

Fixed oil from seeds.—The seeds, after complete separation of the pulp, and subsequent drying, weighed 2828 grams. These were passed through a disintegrator in order to break the shells and expose the kernels (the latter are contained in longitudinal cavities in the shells, and vary in number from 2 to 6 in each seed). Owing to the smallness of the kernels, it was found impracticable to separate them from the shells, and the broken seeds were allowed to stand in contact with cold ethyl ether until all soluble matter had been removed; the ethereal solution was then separated from the seeds, the solvent removed, and 30 grams of a heavy, brown viscous oil of "acidic" odour obtained. The oil possessed the following characteristics:—

$d\frac{15^\circ}{15}$	0.9534
n^{20}_{D}	1.4787
Acid Value	71.5
Saponification Value	194.9
Iodine No. (Wijs, 2 hours)	128.1

Meal.—The dried, finely ground meal possessed a "cereal-like" odour, and a dirty brown colour. A portion of the meal was boiled with water, the liquid allowed to cool and a solution of iodine added; the deep blue colouration produced showed the presence of starch. Microscopical examination of the meal revealed minute granules which were stained blue with very dilute iodine solution. Cellular material other than starch was also observed through the microscope.

Skins.—Beyond drying, grinding (for feeding experiments) and weighing the skins, they were not further examined.

Investigation of Toxic Principle of Fruits.

As previously mentioned, the various portions of the fruit, as well as solvent extracts, were submitted to Mr. R. Grant for the purpose of carrying out feeding tests on guinea pigs; the portion or portions of the fruit which produced poisoning could then be examined carefully with a view to isolating the toxic constituent.

During the period 1923-1928 over one hundred feeding tests were conducted, and in each case where toxic symptoms were observed, or death resulted, the test was repeated on a fresh animal.

Fruit from Trees Growing at Grafton, New South Wales.

The following portions of the fruit were separately administered to the animals, but in no case were toxic symptoms observed:—

Whole fruit (seed broken); skins; meal; kernels of hard seeds; oil from pulp; oil from seed kernels; resin; white nodules separated from ether extract; hot and cold alcoholic extracts of the fruit.

A second parcel of fruit from Grafton gave similar non-toxic results.

Dubbo Fruits.

A viscous extract prepared by treating the fruits with boiling alcohol, and removal of the solvent by distillation under reduced pressure, produced toxic symptoms, and proved fatal. The post-mortem examination revealed evidence that the effects were somewhat similar to those produced by alkaloids of the strychnine type, viz.:—

20/10/26.—3 c.c. alcoholic extract Dubbo (14/10/26) siphoned into stomach at 11 a.m.

21st to 25th, animal active.

26th, animal sick; 27th, animal very sick with slight clonic spasms; 28th, animal in comatose condition; 29th, (9 a.m.) animal dead.

Post-Mortem.—Body rigid; all voluntary muscles deeply congested; spleen slightly so; both kidneys and surface vessels congested; no inflammation of stomach or small intestines; large intestine inflamed; caecum intensely inflamed.

Portion of the concentrated alcoholic extract was successively agitated with ether and chloroform, and after removal of the solvents, the small quantities of extract obtained were used in feeding tests. Both proved to be non-toxic.

Fruit from a Number of Trees Growing at Parramatta.

During the period covering the latter part of 1926, and the full year 1927, many collections of fruit, both ripe and unripe, were made, and experiments to isolate the toxic constituents, carried out.

Ripe fruit.—An extract was prepared, using boiling alcohol as solvent, and the latter was removed under reduced pressure. The dark viscous solution caused toxic symptoms, and death followed in seven days. A post mortem examina-

tion indicated poisoning effects of the strychnine type, and similar to those produced by the Dubbo fruit, viz.:—

20/10/26—3 c.c. siphoned into stomach at 11 a.m.

23/10/26, animal active; 25/10/26, animal sick; 26/10/26, animal very sick. Clonic spasms and rigors similar to those produced by strychnine.

27/10/26, animal dead.

Post-Mortem.—Body rigid, although dead several hours; voluntary muscles all deeply congested; liver congested; spleen slightly so; heart and lungs normal; both kidneys and surface vessels deeply congested; patchy inflammation in pyloric end of stomach; small and large intestines normal; caecum intensely inflamed. Absorption probably takes place in the caecum.

Attempt to Isolate Toxic Constituent.

A portion (1 lb.) of fruits was sterilised in a moist atmosphere in the autoclave at a pressure of 2 lbs. of steam per square inch (in order to destroy enzymes which might decompose alkaloidal substances), the skins broken and the fruits agitated with a mixture of solvents and ammonia, as described by T. A. Henry in "Plant Alkaloids", 1913, p. 180. As a result of the treatment 0.1 gram of a brown amorphous residue with an odour resembling nicotine was obtained, which was dissolved in 1 c.c. of absolute alcohol and siphoned into the stomach of the animal. The material proved non-toxic. A further lot of fruit was similarly treated and a solution of 0.1 gram of the extract in 1 c.c. absolute alcohol allowed to stand until most of the solvent had spontaneously evaporated; it was then diluted to 2 c.c. with saline solution, and 1 c.c. of the liquid injected subcutaneously into the groin of the animal. Toxic effects did not follow.

Treatment of hot Alcoholic Extract with "Floridin Earth."—In order to determine if the toxic constituent might be recovered from the alcoholic extract by selective adsorption, a quantity of extract was prepared by treating 700 grams of the fruit with boiling alcohol, and agitating the cooled solution with a quantity of activated Floridin Earth (XXS grade) on the shaking machine for several hours. The Earth was recovered by filtration, washed with alcohol, and then thoroughly extracted with chloroform. A trace only of residue was obtained after removal of the solvent, which did not produce poisonous effects.

Ethereal Extract of Ripe Fruits.—Since the results obtained gave little indication of the actual source of the toxic constituent, it was decided to conduct feeding tests, using the ether extract of the fruit (which latter had previously been treated with light petroleum ether for removal of the fatty portion of the pulp). The solvent was removed from the ethereal extract and a light brown, tacky resin was obtained. About 0.5 gram was dissolved in 5 c.c. absolute alcohol, and 2 c.c. siphoned into the stomach of a guinea pig. The animal died in 24 hours, the symptoms and effects being similar to those of the previous tests which had proved fatal. The experiment was repeated on another animal with similar results, viz.:

16/3/27. 2 c.c. alcoholic solution siphoned into stomach at 2.25 p.m.; 9 a.m., animal very ill, no specific symptoms; 12 noon, Clonic spasms suggestive of brucine or strychnine poisoning; 2.30 p.m., animal dead.

Post-mortem.—All the muscular tissues had a pink tinge. Heart and lungs normal; large, blotchy haemorrhages in mucosa of cardiac end of stomach, contents of latter frothy and pale green in colour; intestine normal; caecum normal and contents fairly dry, normally they are "sloppy."

Isolation of "Alkaloid".—The ethereal extract (43 grams) was dissolved in 200 c.c. ethyl ether, and agitated with three successive portions of 20 c.c. of 0.5% sulphuric acid solution. The acid liquor was separated and a portion treated with Meyer's solution; a white flocculent precipitate was thrown down, this being the first chemical reaction indicative of an alkaloid obtained since commencing the investigation. After washing with a small quantity of ether, the acid solution was made alkaline with ammonia, and the fluorescent solution agitated with three successive portions of chloroform, separated, and the solvent allowed to spontaneously evaporate. A small quantity of resinous material was recovered which was dissolved in a small quantity of alcohol, and used in feeding tests. The material proved to be non-toxic. Portion of the resin from the above treatment was used in a feeding test and also gave a negative toxicity result.

Unfortunately it was not possible in this case to administer a mixture of the treated resin and the alkaloid (?) owing to the whole of the latter having been used in the feeding test.

Treatment of Ethereal Solution of Resin (After Removal of "Alkaloidal" Body as Above) for Removal of Acid Constituents.

The ethereal solution was washed free from sulphuric acid and agitated successively with the following aqueous solutions:—0.1% sodium carbonate, 1% sodium carbonate and 1% potassium hydroxide. In each case the alkaline extract was separated, washed with ether, and decomposed with dilute sulphuric acid; the liberated acid body was extracted with chloroform, and the solvent removed. In this manner the following products were obtained:—

Extract with 0.1% Na_2CO_3 *Solution.*—1.4% of brown, viscous material of pleasant "acidic" odour.

Extract with 1% Na_2CO_3 Solution.—3.6% dark, viscous, pleasant smelling material.

Extract with 1% KOH Solution.—8.2% dark, viscous material of pleasant odour. Its solution in chloroform exhibited a marked fluorescence.

The ethereal solution of the resin after the above treatment with alkaline solutions was washed free from alkali, and a golden yellow, tacky resin of pleasant odour recovered. A small portion of each of the extracts and the residual resin were used for feeding tests, all of which gave negative results for the presence of toxic bodies.

Unripe Fruits from Parramatta, 22nd March, 1927.

This parcel of fruit was obtained from a tree growing in the grounds of Messrs. Meggitt Ltd., Parramatta, New South Wales. The berries were almost spherical and the skins green, with the exception of a few which showed a slight yellow tinge, indicating the first stage of ripening.

The berries were bruised, and dried in air and sunshine; three pounds of dried fruit were thus recovered from 5lbs. 10ozs. of the fresh fruit (a determination carried out on 100 grams of the fruit by drying at 100° C. showed that the fruit contained 58.5% moisture). They were allowed to stand in contact with cold ethyl ether (previous extraction with petroleum ether was considered unnecessary) for ten days; the solution was poured off, and the solvent removed, when a small volume of green, oily emulsion, containing dark lumps of resinous material, was obtained. The liquid was poured through a filter cloth, the resinous lumps being retained on the filter. Both the oily filtrate and the resin (0.5 gram of each) were separately dissolved in small volumes of alcohol and used in feeding tests. As a result the oily filtrate was non-toxic, whilst the resinous portion killed in 24 hours, viz.:—

11/4/27.—2 c.c. alcoholic solution siphoned into stomach at 2.30 p.m.

12/4/27.—Severe convulsions followed by comatose condition. 12.30 p.m., animal dead.

Post-mortem.—Blotchy haemorrhages in the cardiac mucosa of the stomach; large haemorrhagic areas in the mucosa of the caecum; heart dark and congested; liver slightly pale; other organs normal.

Isolation of "Alkaloidal" Substance.—The remainder of the resin was dissolved in ether, and the solution extracted with successive portions of 0.1% sulphuric acid, a total of 100 c.c. of acid being used. The acid solution was separated, filtered, and on testing with reagents the following reactions were observed:—

Reagent.	*Result.*
Picric acid solution	Slight ppt. on standing.
I in KI	Heavy ppt. at once.
$HgCl_2$ solution	Slight ppt. on standing.
Meyer's solution	Moderate ppt. on standing.
Phosphotungstic acid	Slight ppt. on standing.
Ammonium persulphate	Slight ppt. on standing.

A portion of the acid solution was used in a feeding test, with non-toxic results. A portion (30 c.c.) was almost neutralised with decinormal KOH, the solution concentrated on the water bath almost to dryness, and the residue treated successively with ether and chloroform; practically nothing was dissolved by the solvents, and the aqueous solution was carefully evaporated to dryness on the water bath. The brownish residue, which contained crystals of potassium sulphate, was treated with absolute alcohol and the solution filtered; the solvent was allowed to spontaneously evaporate, leaving a very small quantity of yellowish residue.

Portion of a solution of the residue in alcohol was fed to a guinea pig with non-toxic results.

Since both the resin and the isolated "alkaloid" respectively failed to produce toxic results, it was suggested that a mixture of both might prove toxic. Accordingly 0.5 gram of the "alkaloid free" resin was dissolved in 5 c.c. of alcohol, and mixed with 5 c.c. of the alcoholic solution of the "alkaloid." This solution was used in feeding tests and produced toxic effects similar to those of the original resin.

It was thus apparent that administration of the resin together with the "alkaloidal" substance was necessary to bring about toxic results.

Unripe Fruit from Parramatta, 5th May, 1927.

This collection, from the same tree, represented portion of the same crop obtained in March, 1927. The berries were mostly green, a small proportion only having acquired a yellowish tinge; the pulp of the berries was softer and more "mealy" than that of the March collection. The moisture content was 52.5%. A quantity (15 lbs.), after bruising, was dried in the sunshine, and treated with cold ethyl ether for 8 days. On removal of the ether solution, a brown, aqueous solution separated at the bottom of the vessel. This was apparently derived from moisture remaining in the pulp.

The green ethereal solution was separated, concentrated to small bulk (50 c.c.) and transferred to an open dish, where it set to a gel on cooling. It was allowed to stand for three days, when 13.5 grams of a dark-green, tacky mass, which appeared to consist of a mixture of fat and resin, was obtained. This was dissolved in ether and the solution agitated with 0.1% sulphuric acid solution. The separated acid solution gave a precipitate with Meyer's

solution. The acid solution was almost neutralised with dilute KOH solution, a greenish coloured liquid resulting, which exhibited a blue fluorescence similar to that shown by dilute quinine solution. The solution was concentrated under reduced pressure (temperature not exceeding 60° C.) to about 20 c.c., a dark coloured resinous material, in addition to crystals of potassium sulphate, being deposited on the sides of the vessel. The contents of the vessel were removed with warm water, filtered, and the residue on filter paper, which appeared to consist of meal, washed with small quantities of warm water, these being added to the filtrate. The latter was carefully evaporated to very small bulk on the water bath, a dark resinous material separating out, the whole of which adhered to a glass rod when the liquid was stirred; the aqueous solution containing crystals of potassium sulphate was evaporated almost to dryness, the residue triturated with alcohol, filtered, and the alcohol allowed to spontaneously evaporate; 0.5 gram of brown resinous material being obtained.

The resin adhering to the glass rod was dissolved in alcohol, the solution filtered from adhering potassium sulphate, and the alcohol removed; 0.5 gram of brown resinous material being recovered. In addition to the above, 0.4 gram of resinous material adhering to the bottom of the vacuum distillation apparatus was recovered by washing the vessel with alcohol.

The three lots of "alkaloidal" resin were mixed together by dissolving in 20 c.c. alcohol. The original ether extract, after treatment with 0.1% sulphuric acid, was recovered from the ethereal solution, and 11.5 grams of a greenish-coloured, viscous mass obtained. This was agitated with 100 c.c. alcohol (the resin being dissolved, and the fatty portion remaining in suspension) and 10 c.c. of alcoholic

liquid mixed with 2 c.c. of the "alkaloid" solution; by this means a mixture was obtained which contained the two constituents in the same ratio in which they were present in the original ether extract.

Feeding tests were conducted with (1) 3 c.c. "alkaloid" solution, (2) 3 c.c. "non-alkaloidal" solution, and the abovementioned mixture of both. All three gave negative toxicity results.

Oil from Kernels of above Fruit.—The fixed oil extracted from a quantity of the broken seeds, after removal of skin and pulp, by extraction with ether, proved non-toxic.

Fruit from Tree at Parramatta, 8th July, 1927.

Both ripe and semi-ripe fruit was collected at the same time, and separately treated with ethyl ether. The resulting extracts were used in feeding tests, but in both cases proved to be non-toxic.

Ripe Fruit Obtained from Tree Growing at Richmond, New South Wales.

An ether extract obtained in the manner previously described proved to be non-toxic.

A concentrated alcoholic extract of the fruit was also non-toxic.

Conclusions to be drawn from above Experiments.

As previously mentioned, it would appear that the occurrence of more than one variety of the species would account for the presence of a substance or substances possessing poisonous properties in the fruit from one particular tree, and its absence in another. At the same time, it is apparent that in the variety bearing poisonous fruit, either the method of treatment to obtain the toxic bodies sometimes destroys the active substance, or, alternatively, changes in chemical composition take place in the fruit during the process of ripening.

SUMMARY.

1.—An investigation of the fruit (drupe) of the White Cedar (*Melia Azedarach,* L./var. *australasica* C.D.C.; Syn. *M australasica,* A. Juss) growing in New South Wales was carried out to determine its chemical composition and also to isolate the toxic principle.

2.—Proximate analyses of fruits from trees growing at Grafton, and Dubbo respectively, have been made.

3.—Although incomplete, the results of the examination have revealed an idea of the chemical composition of the oil present in the pulp, the presence of a reducing sugar, dextrose, and the characteristics of a resin extracted by ether. A meal consisting largely of starch was also present in the pulp. The kernels of the hard, ribbed seeds contained a fixed oil.

4.—The results of approximately 100 feeding tests on guinea pigs indicated that a toxic principle was present in the fruit of at least one variety of the species, and further, that the toxic substance occurred in the resinous portion extracted with ethyl ether from both ripe and unripe fruit respectively.

5.—A basic substance of alkaloidal nature has been extracted from the resin by means of very dilute sulphuric acid, which substance and the resin from which it was extracted were non-toxic when used in separate feeding tests. *A mixture of both, however, proved toxic.*

6.—The symptoms of poisoning observed following feeding tests on guinea pigs, and the results of *post mortem* examinations, were similar to those obtained with alkaloids of the strychnine type.

ACKNOWLEDGMENT.

Thanks are due to the following for assistance in obtaining supplies of material:—Forestry Commission of

New South Wales, through the Forest Officers at Dubbo and Grafton respectively; Messrs. Meggitt Ltd., for supplies of fruit from a tree growing in the grounds of their works at Parramatta; and to Mr. Southee, Principal of the Hawkesbury Agricultural College, Richmond, New South Wales.

The Author wishes to express his best thanks to Mr. A. R. Penfold, F.A.C.I., F.C.S., Curator and Economic Chemist, Technological Museum, Sydney, for generous advice and assistance during the progress of the investigation, and also to Mr. E. Cheel, Curator of the National Herbarium, Botanic Gardens, Sydney, for information regarding the botany of the species.

To the Director-General of Public Health, Sydney, thanks are also due for permission to conduct feeding tests at the Department of Public Health, Sydney.

THE CONDENSATION OF $\alpha\beta$-DIBROMOCARBOXYLIC ACIDS WITH BENZENE IN THE PRESENCE OF ALUMINIUM HALIDES.

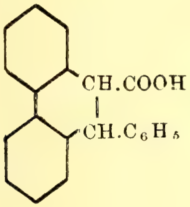
By John Campbell Earl D.Sc., Ph.D.,
and Clive Henry Wilson.

(Read before the Royal Society of New South Wales, Oct. 7, 1931.)

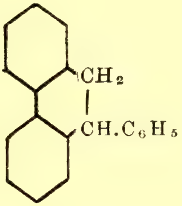
The condensation of trimethylethylene dibromide with benzene in the presence of aluminium bromide yielded $\alpha\alpha$-dimethyl-β-phenylindene (this Journal 1930, *64*, 90), that is, dehydrogenation and ring formation were involved as well as the replacement of the halogen atoms by phenyl groups. It appeared of interest, therefore, to study the behaviour of other dibromo-compounds under similar conditions.

Cinnamic acid dibromide with benzene in the presence of aluminium bromide or ferric chloride gave good yields of $\alpha\beta\beta$-triphenyl propionic acid, m.p. 216.5° uncorr., which has been described previously by Kohler and Heritage (American Chemical Journal 1905, *33*, 156), and Eijkman (Chemisch Weekblad 1908, *5*, 655-666; available in the form of abstract only in J.C.S. abs., 1908, *94*, 796.). With aluminium chloride, however, another acid was obtained (m.p. 148°C.), and this on examination was found to be a derivative of 9-10-dihydrophenanthrene. Distillation of the calcium salt of the acid yielded a hydrocarbon, the analysis and molecular weight of which indicated the composition $C_{20}H_{16}$. On oxidation of the hydrocarbon with chromic acid in glacial acetic acid a substance of the composition $C_{20}H_{14}O$ was obtained, while with aqueous per-

manganate both benzoic acid and phthalic acid were formed. These results are best interpreted by assigning the structures I and II to the acid and the hydrocarbon, respectively.

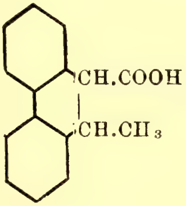


I.



II.

Confirmation of this conclusion was afforded by the application of similar methods to crotonic acid dibromide. In this case, using aluminium bromide, $\alpha\beta$-diphenyl butyric acid (m.p. 188°C.) was produced, while with aluminium chloride a mixture of the same product and another acid (m.p. 127°) was formed. This second acid, on oxidation with chromic acid in the presence of dilute sulphuric acid yielded diphenic acid, and is therefore to be indicated by the structure III.



III

Experimental.

$\alpha\beta\beta$-triphenyl propionic acid (aluminium bromide as condensing agent).

Cinnamic acid dibromide (73 grams) was dissolved in benzene (200 cc.), and aluminium bromide (96 grams) dis-

solved in benzene (50 cc.), was gradually added over a period of one and a half hours. There was a vigorous evolution of hydrogen bromide, and after this had moderated the mixture was heated on a boiling water bath for seven hours.

The product was shaken with concentrated hydrochloric acid, when a thick emulsion was formed, together with a lower acid layer. The emulsion was separated as far as possible and heated under a reflux condenser with a ten per cent. solution of sodium hydroxide. A light brown crystalline solid separated, but was re-dissolved on the addition of more water and heating. The acid was precipitated as a light yellow crystalline solid when the alkaline solution was poured into the hydrochloric acid. The crude product (59 grams) was re-crystallised from hot aqueous alcohol when 47 grams of purified acid melting at 216.5°C. (uncorr.) were obtained.

$\alpha\beta\beta$-triphenyl propionic acid (ferric chloride as condensing agent).

Anhydrous ferric chloride (14 grams), cinnamic acid dibromide (20 grams), and benzene (60 cc.), were mixed and the mixture heated on a boiling water bath for six hours. The benzene solution was washed three times with dilute hydrochloric acid and then with water, after which it was shaken twice with a ten per cent. solution of sodium hydroxide (150 cc.). After decolorising with animal charcoal the alkaline solution was acidified when the acid (16 grams) was precipitated. The crude product melted at 209°C. and after twice re-crystallising from aqueous alcohol its melting point was raised to 215°C.

Ethyl ester of $\alpha\beta\beta$-triphenyl propionic acid.

The calcium salt of the acid (4.5 grams) was suspended in boiling absolute alcohol (40 cc.), and dry hydrochloric

acid gas passed into the boiling solution during three hours. On pouring into water the solid ester (3.6 grams), was precipitated. The crude product melted at 115°C. and, after recrystallisation from alcohol the melting point was raised to a constant value of 119°C. The saponification number of the ester (no. of mgms. of potash required to saponify one gram of the oil) was found to be 170 (calculated for $C_{20}H_{17}COOEt$, 170).

9, 10-dihydro-9-phenyl phenanthrene-10-carboxylic acid.

Powdered aluminium chloride (60 grams) was added gradually to a solution of cinnamic acid dibromide (90 grams) in benzene (400 cc.). After being allowed to stand overnight, the mixture was heated on a boiling water bath for four hours, at the end of which time the evolution of acid fumes had practically ceased.

The resulting benzene solution was washed twice with concentrated hydrochloric acid and subsequently with water, after which it was extracted twice with a ten per cent. solution of sodium hydroxide (100 cc. each time). On acidifying the alkaline solution a semi-solid material separated, which became hard on standing. After recrystallising from hot aqueous alcohol 76 grams of a product melting at 145°C. were obtained. Further recrystallisation raised the melting point to a constant value of 148°C. (uncorr.).

Equivalent weight by titration with standard alkali; found 299, calculated for $C_{20}H_{15}COOH$, 300.

Analysis; found, Carbon 83.9, Hydrogen 5.3 per cent.; calculated for $C_{21}H_{16}O_2$, Carbon 84.0, Hydrogen 5.3 per cent.

The ethyl ester of the above acid.

The ethyl ester was prepared by a similar method to that employed in the case of $\alpha\beta\beta$-triphenyl-propionic acid. The

recrystallised product melted at 116°C., but a mixed melting point with ethyl-triphenyl-propionate (m.p.119°C.) showed a depression to 79°C. Saponification value, found 172, calculated for $C_{20}H_{15}COOEt$, 171.

9-phenyl, 9, 10-dihydrophenanthrene.

The acid (10 grams) from the aluminium chloride condensation was finely powdered and mixed with an excess of soda lime. The mixture was heated in a copper retort until no further product distilled over. The distillate was transferred to a filter and washed first with dilute sodium carbonate solution and then several times with water. The resulting product (1.4 grams) after recrystallisation from alcohol melted at 121.5°C.

Found, Carbon 93.7, Hydrogen 6.3; calculated for $C_{20}H_{16}$, Carbon 93.7, Hydrogen 6.3 per cent.

Molecular weight, found (by Mr. R. A. Wallace), 259; calculated 256.

Oxidation of the Hydrocarbon.

(a) With chromic acid in glacial acetic acid.

The hydrocarbon (1.9 grams) was dissolved in glacial acetic acid (25 cc.) and chromic acid (10 grams) gradually added. The solution was boiled under a reflux condenser for 10 minutes, after which it was poured into water. The separated oil was extracted with benzene, and the benzene solution shaken with a 10 per cent. solution of caustic soda. The washed and dried benzene solution, after evaporation, yielded an oil which crystallised on standing. The crude product (1.1 grams) melted at 103°C., and on recrystallisation from ligroin the melting point was raised to a constant value of 105-106°C.

Found, Carbon, 88.3, Hydrogen 5.2 per cent.; calculated for $C_{20}H_{14}O$, Carbon 88.8, Hydrogen 5.2 per cent.

(b) With potassium permanganate.

The hydrocarbon (2 grams) was mixed with a solution of potassium permanganate (2 grams) in water (400 cc.), and the mixture was boiled under a reflux condenser until all the permanganate had been reduced. The solution was filtered and again boiled with two successive quantities of 2 grams of potassium permanganate, the last portion being not completely reduced. The excess of permanganate was destroyed with sodium bisulphite, and the solution acidified and extracted with ether. From the ethereal extract 0.4 grams of benzoic acid were isolated. The aqueous solution was neutralised and evaporated to small bulk and again acidified, when 0.42 grams of a solid material, identified as phthalic acid, were obtained.

$\alpha\beta$-Diphenylbutyric acid.

$\alpha\beta$-Dibromobutyric acid (4 grams) was dissolved in benzene (150 cc.), and aluminium bromide (7 grams) added. The mixture was heated on a boiling water bath for six hours, after which it was washed twice with concentrated hydrochloric acid and subsequently with water. The benzene solution was then shaken with two successive quantities (50 cc.) of 10 per cent. caustic soda solution, from which the acid (3.1 grams) was precipitated by the addition of hydrochloric acid. On recrystallisation from aqueous alcohol, 2.7 grams of the pure acid, melting at 187°C., were obtained. Equivalent by titration, found 237.5, calculated for $C_{15}H_{15}COOH$, 240.

9, 10-dihydro-9-methyl phenanthrene-10-carboxylic acid.

$\alpha\beta$-Dibromobutyric acid (15 grams) was dissolved in benzene (250 cc.) and aluminium chloride (20 grams) added. After heating on a boiling water bath, the product was treated as in the previous experiment, 10.5 grams of a crude acid material being obtained. This was separa-

ted into two fractions by crystallisation from alcohol, the less soluble portion (2.1 grams) being identified as $\alpha\beta$-diphenylbutyric acid (mpt. 188°C.). The more soluble portion (4.5 grams), on repeated crystallisation, attained a constant melting point of 127°C.

Found, Carbon 80.6, Hydrogen 5.8 per cent.; calculated for $C_{16}H_{14}O_2$, Carbon 80.6, Hydrogen 5.9 per cent.

Equivalent, found, 235; calculated for $C_{15}H_{13}COOH$, 238.

Oxidation of the above acid.

The acid (2 grams) was mixed with water (300 cc.) and sulphuric acid (15 cc., concentrated), and to the mixture chromic acid (25 grams) was added, the whole being boiled under a reflux condenser for 4 hours. After standing overnight, the insoluble material was filtered off and treated with ammonia. The ammoniacal solution was filtered and acidified with hydrochloric acid, when a white precipitate (1.78 grams) separated. The crude material melted at 221°C.; after two recrystallisations from water, the purified product melted at 227°C., and showed no depression of melting point when mixed with an authentic sample of diphenic acid.

The authors' thanks are due to Mr. S. L. Leach, B.Sc., for assistance in the experimental work described in this paper.

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THE ESSENTIAL OIL OF *LEPTOSPERMUM LIVERSIDGEI*, VARIETY B., AND THE OCCURRENCE OF ISOPULEGOL.

PART I.

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(*Read before the Royal Society of New South Wales, Nov.* 4, 1931.)

In a paper entitled "Observations respecting some essential oils from *Leptospermum Liversidgei*," published in the Journal and Proceedings of the Royal Society of New South Wales, Volume LVI (1922), pages 80-87, the author directed attention to the probable occurrence of several forms of *Leptospermum Liversidgei* as evidenced by the composition of the essential oils. Field observations conducted since that date have confirmed the views then expressed. Numerous distillations of essential oils from the leaves and terminal branchlets collected from various parts of Queensland and New South Wales supported by field investigations have shown a similar occurrence of physiologic forms to that reported in the case of *Eucalyptus dives*. (See this Journal, Vol. LXI (1927), pages 54-67.) The oil obtained from Variety B. was found to contain citronellal in quantity (no citral) and thus differed considerably from the Type which contained the aldehyde citral instead.

The aldehyde content was determined by the bisulphite method, and for the reasons set forth in the paper entitled "The Estimation of Citronellal and Citral in Australian Essential Oils," published in the Journal and Proceedings

of the Sydney Technical College Chemical Society, Volume 4, pages 53-60, it was found necessary to redetermine the citronellal content by more reliable and accurate methods. The re-examination by these new methods, and particularly the Holtappel method, as modified by Penfold and Arneman (l.c.), shows the actual aldehyde content to be from 33-42%, as per results shown in Table "A." It was apparent, therefore, that the difference in the results obtained between the modified Holtappel method and the bisulphite method was due to the presence of an unidentified substance, most probably a closely related alcohol which was absorbed in the bisulphite liquor and estimated as aldehyde, as mentioned on page 55 of aforementioned publication. A careful examination revealed the presence of isopulegol, which according to J. L. Simonsen ("The Terpenes," volume 1, page 254) has not been found to occur in nature. Although citronellal is readily converted into isopulegol, yet the evidence adduced in this investigation proves beyond all doubt the natural occurrence of this alcohol in the freshly distilled oils. The isolation and identification of isopulegol, both free and combined, in this particular oil is the first authentic record of its natural occurrence.

There still appears to be a further unidentified constituent, as the quantity of isopulegol isolated, together with the citronellal as determined, plus the sesquiterpene alcohol, falls considerably short of the total amount of acetylisable constituents. This body is now being sought and the results of the further investigation of this oil will be made available at a later date.

Essential Oils.

The essential oils were of a pale yellow to brown colour, moderately mobile, with a pronounced odour of citronellal. Nearly 2,000 lbs. weight of the leaves and terminal branch-

lets, cut as for commercial purposes, on subjection to steam distillation, gave an average yield of 0.5% of oil. The identity of *d*-*a*-pinene and citronellal, as previously reported, were confirmed, whilst the occurrence of isopulegol, together with a sesquiterpene alcohol and their caprylic and caproic acid esters has now been established.

Experimental.

The leaves and terminal branchlets of Variety B., cut in all instances as for commercial distillation, and obtained principally from the Coraki District of New South Wales, yielded, on distillation with steam, crude oils possessing the chemical and physical characters as shown in accompanying Table "A."

Every consignment was separately examined, but for the purposes of this communication the results for the last consignment only are recorded.

300 c.c. of crude oil, 30/6/'31, were distilled at 10 mm. with the following results, viz.:—

No.	Boiling Point	Volume	$d_{15}^{15°}$	$a_D^{20°}$	$n_D^{20°}$	Aldehyde Content
1	48-55°	17 c.c.	0.8622	+ 37.3°	1.4654	13%
2	56-80°	16 c.c.	0.8689	+ 23.0°	1.4611	37%
3	80-95°	196 c.c.	0.8813	+ 9.3°	1.4604	53%
						Ester No.
4	95°(10 mm.)-115°(5 mm.)	15 c.c.	0.9151	+ 8.75°	1.4763	82
5	115°(5 mm.)-130°(5 mm.)	14 c.c.	0.9509	+ 8.75°	1.4875	52

Determination of d-*a*-*pinene.*

The presence of pinene in the first and second fractions was determined in the first communication referred to by the preparation of the nitrosochloride. It was deemed advisable to confirm the presence of this terpene in Fraction No. 1 by removing small quantities of the aldehyde with sodium bisulphite solution. The treated oil was then washed with water, dried and distilled over metallic sodium at 764 mm. The major portion of the

oil distilled at 154-156° (764 mm.) and had $d_{15}^{15°}$ 0.8621 $\alpha_D^{20°}$ +40° $n_D^{20°}$ 1.4646. Oxidation with potassium permanganate resulted in an excellent yield of pinonic acid, which after purification from petroleum ether (boiling point 50-60°) melted at 70°.

0.5170 gram in 10 c.c. chloroform gave a polarimeter reading of +4.6°, $[\alpha]_D^{20°} = +89$.

Determination of citronellal.

The amount of citronellal in fraction No. 3 was found to be 53%. A sample of the aldehyde purified through the bisulphite compound gave the following chemical and physical constants, viz. :—

Boiling point 88-91° (10 mm.) $d_{15}^{15°}$ 0.8611 $\alpha_D^{20°}$ +10.1 1.4484.

The semicarbazone prepared therefrom melted at 82.5°.

Determination of isopulegol.

50 c.c. of fraction 3 were heated with an equal weight of phthalic anhydride in benzene solution for eight hours on a boiling water bath. (Only a small quantity of isopulegol is produced from pure citronellal under similar conditions.) The phthalic acid ester prepared therefrom was treated with excess of 25% sodium hydroxide solution and the liberated alcohol blown over with steam. The water-white distillate possessed the characteristic odour of isopulegol, which resembles very closely that of menthol. On distillation it boiled at 92-94° (10 mm.) and had $d_{15}^{15°}$ 0.9199 $\alpha_D^{20°}$ − 1.75° $n_D^{20°}$ 1.4702. Many samples of this alcohol were prepared from the various consignments of oils and gave the following range of constants, viz. :—

Boiling point 92-94° (10 mm.) $d_{15}^{15°}$ 0.9162-0.9189 $\alpha_D^{20°}$ − 1.1° to − 6.1° $n_D^{20°}$ 1.4702-1.4730.

It is of interest to record that samples of isopulegol prepared from the crude oil immediately after distillation were found to have a much higher specific gravity than when prepared through fraction No. 3 distilling between 80-95° (10 mm.). The chemical and physical characters of such preparations were as follows, viz.:—

Boiling point 93-94° $d\frac{15^\circ}{15}$ 0.9221-0.9228 $\alpha_D^{20^\circ}$ -1.3° to -5.6° $n_D^{20^\circ}$ 1.4716-1.4728.

In the absence of definite evidence it is assumed that the higher specific gravity is due to contamination with small quantities of other alcoholic bodies, most probably darwinol. The evidence in support of this statement was obtained when small quantities of alcohols isolated from the higher boiling fractions were examined. These were found to contain isopulegol, together with an unidentified alcohol which had a rose-like odour. In view of the high specific gravity it can only be attributed to darwinol and not to geraniol or citronellol.

The identity of the alcohol with isopulegol was obtained by the preparation of various derivatives. On treatment with cyanic acid a good yield of allophanate was obtained of melting point 219°-220°. Simonsen in "The Terpenes," volume 1, states that this alcohol can be characterised by this derivative. The writer, however, has found that the napthylurethane is very characteristic. On allowing equimolecular proportions of isopulegol and napthylisocyanate to remain in contact at room temperature combination resulted in less than twelve hours. This excellent derivative on purification from methyl alcohol melted at 112-113°.

0.1 gram on combustion gave 0.2857 gram CO_2 and 0.0693 H_2O.

$C = 77.92\%$ $H = 7.7\%$

$C_{10}H_7$ $NHCOOC_{10}H_{17}$ requires $C = 78.02\%$,
$H = 7.74\%$

Many combustion determinations made on the purified alcohol during the past two years gave unsatisfactory results, the carbon estimations being always low. The results, therefore, are not recorded.

The identity of the alcohol with Isopulegol was confirmed beyond all doubt by its oxidation to isopulegone.

16 c.c. of the alcohol having $d\frac{15^\circ}{15}$ 0.9189 $a_D^{20^\circ} - 1.1^\circ$ $n_D^{20^\circ}$ 1.4724 were treated with 160 c.c. of Beckmann's chromic acid mixture at room temperature when 10 c.c. of a ketone possessing the following chemical and physical characters was isolated, viz.:—

Boiling point 96-98° (10 mm.) $d\frac{15^\circ}{15}$ 0.9623 $a_D^{20^\circ} - 4.45^\circ$ $n_D^{20^\circ}$ 1.4691.

The following derivatives of the ketone were obtained, viz.:—

1. (a) A semicarbazone of melting point 173° with a specific rotation in chloroform solution of − 29.41° (20°).

   (b) A semicarbazone of melting point 147-148° with a specific rotation of + 36.5 (20°).

2. (a) An oxime of melting point 133-134°, optically inactive in chloroform solution.

   (b) An oxime of melting point 124° with a specific rotation in chloroform solution of + 14.9° (20°).

It is worthy of note that the best yields and quality of isopulegol were obtained when the phthalic acid ester was

prepared by prolonged treatment in benzene solution on the boiling water bath. Heating in an oil bath at 140° for four hours resulted in a considerably diminished yield of alcohol.

Determination of the esters present in fractions 4 and 5.

These fractions were saponified with normal alcoholic potassium hydroxide solution at room temperature. In this way 7 c.c. of liquid acids were obtained which behaved as follows on distillation, viz:—

1st drops 245° at 768 mm.
Between 245-252° 2 c.c.
Between 253-270° 3½ c.c.

On account of the comparatively small quantities and the slight decomposition it was decided to convert portion of them to their silver salts.

0.4650 gram silver salt of the first fraction gave on ignition 0.1846 gram Ag. Ag. = 40.47%.

0.4709 gram of silver salt of second fraction similarly treated gave 0.2885 Ag. Ag. = 38.94%.

These results point to the acid consisting principally of caprylic acid, the silver salt of which would yield on ignition 38.71% Ag.

A small amount of silver salt prepared from the aqueous acid gave the following results on examination, viz.:—

0.0620 gram on ignition gave 0.0279 gram Ag.
Ag. = 45%.

The silver salt of caproic acid on ignition would yield 48.43% Ag.

Computing from these results and taking into account the boiling point range of the mixed liquid acids, the writer is of the opinion, on the evidence available, that they con-

sist of a mixture of caprylic and caproic acids, the former predominating.

The residual oil after saponification was treated with phthalic anhydride in benzene solution for a prolonged period, but only a very small quantity of alcohol was regenerated from the phthalic acid ester produced. Two preparations resulted as follows, viz.:—

(a) $d\frac{15^\circ}{15}$ 0.9028 $\alpha_D^{20^\circ}$ $\pm 0^\circ$ $n_D^{20^\circ}$ 1.4668 (4 c.c.)

(b) $d\frac{15^\circ}{15}$ 0.9253 $\alpha_D^{20^\circ}$ $\pm 0^\circ$ $n_D^{20^\circ}$ 1.4690 (2 c.c.)

Both were found to consist of a mixture of isopulegol with an unidentified alcohol which, on account of its high specific gravity and odour, appears most likely to be darwinol.

The remainder of the oil, after treatment with phthalic anhydride, gave 16 cc. distilling between 140° and 170° at 20 mm. It had $d\frac{15^\circ}{15}$ 0.9477 $\alpha_D^{20^\circ}$ $+5.5^\circ$ $n_D^{20^\circ}$ 1.4902, and was found to consist essentially of an unidentified sesquiterpene alcohol accompanied by small quantities of sesquiterpene.

Determination of alkali soluble bodies.

The crude oils, on treatment with 8% sodium hydroxide solution yielded under 1% of alkali soluble bodies. The quantities isolated were too small for definite identification, but from their general physical characters and deportment appeared to be a mixture of eugenol with citronellic acid.

My thanks are due to Mr. F. R. Morrison, F.C.S., A.A.C.I., Assistant Economic Chemist, for much assistance in this investigation, and to Mr. P. T. Aubin, District Forester at Coraki, New South Wales, for his help in procuring the various supplies of plant material.

Essential Oils from leaves of *LEPTOSPERMUM LIVERSIDGEI*—Variety "B."

Date.	Source of Material.	Weight of Leaves.	Yield of Oil.	$d\frac{15^\circ}{15}$	$\alpha_D^{20^\circ}$	$n_D^{20^\circ}$	Solubility in 70% Alcohol (by weight)	Ester No. 1½ hours hot sap.	Ester No. after Acetylation	Aldehyde Content.	Method of Aldehyde determination
26/9/1922	Stradbroke Island, Q.	78 lbs.	0.64%	0 8831	+9.4°	1.4609	1,6 vols	—	—	75%	Bisulphite method
15/10/1926	Woodburn, N.S.W.	193 lbs.	0.62%	0.8985	+9.5°	1.4665	1.2 ,,	44.0	260	31%	Oximation
11/4/1929	Bonalbo, N.S.W.	173 lbs.	0.46%	0.8900	+13.4°	1.4665	1,6 ,,	43.0	244	33% 26%	Modified Holtappel Oximation
18/9/1929	do.	1154 lbs.	0.41%	0.8960	+11.25°	1.4682	1.4 ,,	—	—	38%	Modified Holtappel
30 6/1931	do.	394 lbs.	0.4%	0.8936	+11.7°	1.4662	1.4 ,,	47	255.3	41.4%	do. do.

NOTES ON THE PERICALYMMAE SECTION OF THE GENUS *LEPTOSPERMUM* (WITH DESCRIPTIONS OF THREE NEW SPECIES).

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In the Journal and Proceedings of this Society (1918-1923) I have already submitted for consideration descriptions and notes on six species and one variety of the genus *Leptospermum.* In the present paper I propose to give a brief outline history of the genus and the sections which have been raised to generic rank by certain authorities, more particularly in connection with the Section Pericalymma, the species of which seem to be much more widespread over Australia than has hitherto been recorded.

The genus *Leptospermum* was originally established by the Forsters (1776), who published a description and gave details of certain characters of seven species of Myrtaceous plants, together with text-figures of four of these, including *Leptospermum scoparium,* native of New Zealand, commonly known as "Manuka" or "Tea-tree," which is generally regarded as the type of genus. Four of the species enumerated in the above work have since been transferred to *Metrosideros,* one to *Melaleuca,* and the other to *Baeckea.* It is interesting to note that one of the Forsters, in a subsequent work (Geo. Forster, 1786), transferred the species of *Leptospermum scoparium* to *Melaleuca,* and he was followed by Wendland (1819), but

so far as I can ascertain, no valid reasons were given for this change. Robert Brown (1831) seems to have had a very clear conception of the plants allied to the type species of what is commonly accepted as *Leptospermum*, for we find that he made the following statement:—"*Leptospermum*, of which nearly thirty Australian species have been observed, exists also in New Zealand and in the Moluccas. In Terra Australis its maximum is decidedly in the principal parallel, and, like *Melaleuca*, it is much more abundant in the southern region than within the tropics."

DeCandolle (1828) enumerated twenty-six species of *Leptospermum*, including three which he classed under a section as *Agonis*. Don (1832) did not take up the name *Agonis*, but enumerated the three species of DeCandolle's section *Agonis* under *Billotia*. The names *Billotia* of Don and *Billottia* of R. Brown (1832) were not taken up by Bentham and other workers, probably on account of a Rubiaceous plant being recorded by Colla (1825) as *Billiota*. Bentham (1866) established the sectional name Agonis of DeCandolle as a genus, and set up two sections, viz.: *Taxandria*, with 10 stamens regularly opposite the calyx-lobes and petals, ovules 2 in each cell; and *Ataxandria*, with 20 to 30 stamens, non-opposite the centre of the petals, ovules 4 to 6 in each cell. Ten species are enumerated under the genus *Agonis* by Bentham (l.c.), all of which are from Western Australia, and are easily recognised by the flowers being densely packed in globular heads, besides the other characters referred to above.

Bentham (1866) enumerated 20 species and 15 varieties, which were classed under three sections, based chiefly on the number of cells and the shape and size of the seeds

contained in the capsules, which may be characterised as follows:—

Fabricia—Capsules 6 to 10 celled. Seeds few, the fertile ones comparatively broad and acutely angular, or more or less winged.

Euleptospermum—Capsules usually 5-celled or rarely reduced to 4 or 3 cells. Seeds all narrow-linear, the fertile seeds scarcely distinguishable from the infertile seeds.

Pericalymma—Capsules 3-celled, or very rarely 4-celled. Ovules 4 to 8 in each cell, the fertile seeds more or less cuneate and usually twice the size of the infertile ones.

In a subsequent work, when commenting on these characters, Bentham (1869, p. 135) remarked that he "regarded the differences in the structure or shape of the seeds as a sectional rather than a generic character."

Bentham also regarded the characters of the numerous species of *Leptospermum* as exceedingly vague and variable, and stated that "they appear all to be connected by an almost infinite series of intermediate gradations." Bentham further remarked (l.c.) "that he found the genus in a singular state of confusion. In the first place it long formed a common receptacle for all capsular Myrtaceae with small coriaceous leaves and numerous short stamens. Again, a few common species, scarcely distinguishable by any positive characters, are yet so polymorphous, especially in our gardens, as to have been enormously multiplied by horticultural botanists, whilst almost all those which showed any tangible specific differences have been at various times proposed as distinct genera. And, lastly, notwithstanding the facility of examining living material of several species common in our plant houses, errors in

some of the important characters originally misunderstood have been servilely copied by almost all modern botanists."

The three sections as defined by Bentham (1866) form natural, easily recognised groups, especially if the mature seeds be taken into account. Although the section Pericalymma was established by Endlicher (1837), based chiefly on the 3-celled ovary and a reduced number of ovules in each cell, Schauer (1844-45) seemed to regard this of sufficient importance to raise the sectional name to generic rank, but Baillon (1880) and Nidenzu (1893) followed, in the main, Bentham's classification.

It is interesting to note that, in a general review of the characters of certain Leptospermoideae, Bentham (1869) observed that the characters of *Pericalymma* also occurred in two species of Euleptospermae with numerous ovules (i.e., *L. abnorme* and *L. Roei*). It is chiefly owing to the extreme variation of the forms of leaf, the degree of pubescence and the variable number of cells in the ovaries that so much confusion has been created in the nomenclature of this genus. This, no doubt, has arisen owing to the small number or fragmentary nature of the specimens upon which some of the species, as well as genera, were founded, and probably also because of the difficulty of specific determination due to the original description being inadequate as well as to the literature being scattered.

In this regard, we may review *Leptospermum abnorme* F.v.M. Herb. of Bentham. The specimens on which this species was founded were collected by Dr. Herman Beckler on the Hastings River in New South Wales, and originally described by Mueller (1860) under the name *Kunzea brachyandra.* It appears, however, that Mueller afterwards changed the name in the herbarium to *Leptospermum abnorme,* which was adopted by Bentham (1866),

who records A. Cunningham and J. Dallachy having also collected specimens of the species from the same locality. In addition to the Hastings River specimens, Bentham (l.c.) also records the species from Severn River, N.S.W., collected by C. Stuart; Northumberland Island (R. Brown) and Duck Creek, Queensland (J. Dallachy), and Port Essington, North Australia (Armstrong). In the National Herbarium, Sydney, there are specimens from the Endeavour River (collector?) ex herbarium, Brisbane, which in no way differ from the Hastings River and Port Essington specimens. There are also specimens from the Finis River, Northern Territory, collected by W. S. Campbell, who states that "it looks like *Agonis,* and is locally known as 'Weeping Tea Tree.'" The Finis River specimens have rather long leaves, more or less covered with a silky down of a silver colour, but are narrower than the Port Essington and Endeavour River specimens. White and Francis (1920) have transferred the Endeavour River specimens to *Agonis* as a new species under the name *A. longifolia.*

The chief characters on which they have founded the species are the longer leaves and puberulent calyx-tube. Having examined a very large series of specimens, collected over a very wide area of the northern parts of New South Wales, viz., Wauchope, Port Macquarie, Woodford Island, Copmanhurst, Wilson's Downfall, Grafton to Dalmorton, Casino, Tooloom River, Tenterfield and Ballina, as well as a series of specimens from the following localities in Queensland—Silverwood and Crow's Nest, Darling Downs, Stradbroke Island, Blunder Creek, Freshwater Creek, Redcliffe and Maryborough, I am unable to draw any sharp line of distinction between the original *Kunzea brachyandra* of Mueller (which includes *Leptospermum abnorme* F.v.M. Herb. of Bentham) and the *Agonis*

abnormis and *Agonis longifolia* of White and Francis. The plants belonging to the above species, together with those of *Agonis elliptica* White and Francis, and *Agonis elliptica* var. *angustifolia* White and Francis (1920), have the characteristic 3-valved capsules and more or less cuneate or oblong fertile seeds intermixed with narrower infertile ones, as is seen in the section Pericalymma.

In view of this, I suggest that these plants be classed as follows:—

Leptospermum (Sect. Pericalymma) *brachyandrum* nov. comb. (*Leptospermum abnorme* F.v.M. Herb. Benth.) (*Agonis abnormis* and *A. longifolia* White and Francis).

Leptospermum (Sect. Pericalymma) *Whitei,* nov. comb. (*Agonis elliptica* White and Francis). The specific name *elliptica* is already preoccupied for a species of *Leptospermum,* hence it is proposed to dedicate this rather distinctive series of plants to Mr. Cyril Tenison White, Government Botanist of Queensland, who has done so much towards the investigation of the flora of Queensland.

The Rev. B. Scortechini (1881-2), in commenting on some plants collected at Stradbroke Island, which he listed under *Leptospermum abnorme,* F.v.M. Herb., stated that "it is with some hesitation that I introduce this plant into the South Queensland flora. Its characters do not altogether answer the description of the typical *L. abnorme.*"

I have not seen the specimens referred to by Scortechini, but suggest that they may belong to the proposed new combination, *Leptospermum* Whitei Cheel (*Agonis elliptica* (White and Francis) or the var. *angustifolia* of the latter, which show several transitory forms between

L. brachyandrum (F.v.M.) Cheel, and *Agonis Scortechiniana* F.v.M., which incidentally is referred to by Woolls (1889), who says that "it is described by Baron von Mueller as being a remarkable species, extending the limits of the genus (*Agonis*) to the eastern coast."

With regard to *Agonis Scortechiniana*, it would appear at first sight to be correctly classed in its proper genus, but when carefully examined it will be noted that the flowers are not closely packed in dense globular heads, as in the whole of the species of the genus, as found in Western Australia, but rather in axillary clusters or terminal corymbose-racemes.

The individual flowers of *Agonis Scortechiniana*, as well as those of the closely allied species *Leptospermum Whitei* (*Agonis elliptica* and var. *angustifolia*), are not strictly sessile, but are shortly pedicellate, and although in the early stage of development are crowded together in the numerous brown, scarious, or more or less woolly bracts, when fully developed are seen to be in more or less loose fascicles of 2 to 5 flowered cymes. Plants of several other species of the genus *Leptospermum* have the flowers arranged in clusters or fascicles. The most noteworthy of these are *L. stellatum*, *L. attenuatum* and *L. podanthum*. In this group, however, the pedicels are much more elongated. The capsules and seed characters of the two groups, viz., those with the flowers arranged in clusters with very short pedicels, and those with the flowers arranged in clusters with elongated pedicels, are very much the same and will form the subject of a separate paper which is now being prepared for the purpose of linking up several other species, including *Leptospermopsis* s. le Moore (1920), with the Section Pericalymma.

Leptospermum trivalvum, sp. nov.

Frutex gracilis, 1-3 m. altus, ramis plus minusve pilosis, voliis aliquantum fascicularibus, acutis, 3 aut interdum 5 nervatis. ad 4-7 mm. longis, 1.5-2.5 mm. latis, foliis junioribus aliquantum argenteo-tomentosis, glabrecentibus; floribus albis axillaribus solitariis, tubo calycis 3-4 mm. lato, ad basim vix attenuato, sericeo-tomentoso, lobis 1-2 mm. longis, glabris sed glandulis punctatis, petalis suborbicularibus, ovario pubescente, 3 loculari, stylo 1.5-2 mm. longo, stigma minute capitata; fructibus 3-3.5 mm. latis valvis tubum vix excedentibus; seminibus fertilibus paucis plus minus ve cuneatis.

Slender shrub, varying from 3 to 8 feet high, branches and twigs more or less covered with silky hairs. Leaves somewhat clustered, lanceolate and slightly convolute at the apex, acute, 3-veined or occasionally 5 prominent veins, the larger leaves 4 to 7 mm. long, 1.5 to 2.5 mm. broad, the others in each cluster smaller, somewhat silvery-tomentose when young, becoming glabrous with age. Flowers white, singly in each cluster of leaves or axillary when the leaves are not clustered. Calyx-tube 3-4 mm. diameter, slightly tapering at the base, silky-hairy, the lobes 1 to 2 mm. long, glabrous, but dotted with oil-glands. Petals sub-orbicular, twice as large as the sepals, or in luxuriant plants larger. Ovulary pubescent, 3-4 celled. Style 1.5 to 2 mm. long. Stigma minutely capitate. Fruits about 3 to 3.5 mm. diameter, the valves slightly exceeding the calyx-tube. Fertile seeds few, comparatively large, more or less well shaped, intermixed with smaller, narrower, infertile ones.

This is an interesting species, usually found on sandy or quartzite mountains or ridges in the southern and western parts of the State of New South Wales. It has somewhat the appearance of *L. arachnoideum* in the herbarium, but in the field it has quite a different habit, being more upright, and the leaves are broader and more silvery.

It has previously been confused with *L. arachnoideum*, *L. myrtifolium*, *L. myrsinoides* and *L. attenuatum*, but is abundantly distinct, being constantly 3-celled, whereas all the others are normally 5-celled (except *L. myrsinoides*, which varies from 4 to 5), and the seeds place it in the Pericalymma Section, whereas the fertile and infertile seeds of *L. arachnoideum*, with which it has mostly been compared, are all narrow and slender, characteristic of the Euleptospermeae.

Dubbo to Tomingley, J. H. Maiden, September, 1898, and E. Cheel, October, 1930. Type. Other localities are: Dubbo to Gilgandra (W. Forsythe, October, 1901); Wyalong (J. L. Boorman, September, 1918); Wyalong (R. H. Cambage, No. 113, September, 1900); Gilgandra (G. A. Withers, November, 1925); Bogan Gate (K. Walker, June, 1908; E. H. Ising, No. 2171); Warrumbungle Ranges (W. Forsythe); Ardlethan (R. H. Cambage, No. 4212); Harvey Ranges, Peak Hill (J. L. Boorman); Nymagee (R. H. Cambage, 4464); Barellan (W. Bourke); Cobar (Archdeacon Haviland); Hill End (R. H. Cambage, No. 2768); Fifield (R. H. Cambage, No. 1949); Lachlan River (J. Duff, 1882); Ilford to Rylstone (E. Cheel); Orange and Parkes (Dr. McGillivray, per A. Morris, No. 1117); Yass (Rev. J. W. Dwyer); Bowan Park, near Cudal (W. F. Blakely); Yalgoblin (J. L. Boorman); Bumberry (Dr. J. B. Cleland); Queanbeyan (R. H. Cambage, No. 3370); Gilmore to Tumut (J. L. Boorman). A specimen from Black Mountain, west of Queanbeyan (R. H. Cambage, No. 3091) has fruits tapering at the base into slender pedicels, which are perfectly glabrous, and may not belong to this species. There are also specimens from Mitta Mitta River, Victoria (ex Williamson's Herb. No. 1657) collected by S. Clinton.

LEPTOSPERMUM SEMIBACCATUM, sp. nov.

Frutex virgatus, 1-2 m. altus, foliis juvenilibus virgisque sericeo-hirsutus, glabrescentibus, foliis adultis plus minusve glabris, planis, ellipticis vel oblongo-lanceolatis, 6-14 mm. longis, 3 mm. latis, 3-5 nervatis, bracteis imbricatis fuscis marginibus fimbricatis flores circumdatis, calycis tubo minute hirsuto, glabrescente, primo plus minusve succulento deinde aliquantum sicco et rugoso, sepalis 1.5 mm. longis acutis, ovario 5-loculari ovulis paucibus, capsularibus sessilibus 3-4 mm. latis, valvis tubum vix excedentibus.

Shrub with several whip-stick-like stems springing from the base, usually 1-2 M. (4 to 5 feet) high or rarely more than 2 M. (7 feet). Bark more or less fibrous. Juvenile leaves and twigs silky-hairy, but disappearing with age, so that the fully-developed leaves are almost glabrous. Leaves plain, elliptical to oblong-lanceolate, 6-14 mm. ($\frac{1}{4}$ to $\frac{1}{2}$ inch) long, 3mm. ($\frac{1}{8}$ inch) wide, 3 to 5 nerved. Flowers enclosed, with brownish-coloured imbricate bracts with fimbriate margins. Calyx-tube minutely silky-hairy, but almost glabrous with age, at first somewhat softly-succulent and berry-like, drying up and much wrinkled with age. Sepals 1.5 mm. ($\frac{1}{16}$ inch) long, acute. Ovary 5-celled, with few ovules. Capsules sessile, 3-4 mm. ($\frac{3}{16}$ inch) diameter, the valves very slightly exceeding, or more often level with, the rim of the calyx-tube.

An interesting plant with fruits more or less succulent and somewhat resembling those of *L. glaucescens* Schauer, which is united with *L. lanigerum* by Bentham and others as a synonym, but which is abundantly distinct from that species, as I will endeavour to show when dealing with the *lanigera* series.

The original specimens of this species were collected on Wallis Island, Tuncurry, in May, 1925. The plants were in the fruiting stage, with a few flowers in the early bud stage, but no fully-developed flowers were present. Speci-

mens have since been collected by Mr. C. T. White on Moreton Island, Moreton Bay, in Queensland, also in the fruiting stage, so that I am unable at present to describe the petals, stamens and style.

Leptospermum sphaerocarpum, sp. nov.

Frutex virgatus, 1-2.5 m. altus, foliis 6-10 mm. longis, 2-5 mm. latis, lanceolatis acutis, juvenilibus aliquantum hirsutis glabrescentibus, obscure 3- nervatis, floribus solitariis terminalibus bracteis scariosis fuscis circumdatis, tubo calycis leviter hirsutis, lobis acutis plus minus ve sericeo-hirsutis vel tomentosis, petalis orbicularibus albis, circiter 5 mm. latis, staminibus 25-30, capsulis maturis plus minus ve sphearicis, 3-vel nonnunquam 4-locularibus, valvis sphaerico-convexis, seminibus linearibus circiter 5 mm. longis.

Shrub, with upright, slender, loose branches, from 4 to 8 feet high. Leaves 6 to 10 mm. long, 2 to 5 mm. broad, lanceolate, acute, slightly hairy in the juvenile stage, glabrous with age; venation not prominent but obscurely 3-nerved; oil glands more or less porose-punctate. Flowers singly terminal on the young branchlets, surrounded with several scarious brownish-coloured bracts. Calyx-tube slightly hairy, lobes acute, more or less covered with short silky hairs or down. Petals orbicular, white, about 5 mm. diameter. Stamens 25 to 30, almost as long as the petals. Style short, with a capitate stigma. Capsule somewhat turbinate, but when fully matured spherical, normally 3-celled, but occasionally 4-celled, the valves much domed before finally opening to shed the seeds, which, both fertile and infertile, are linear and about 5 mm. long.

An exceedingly interesting plant, flowering during October, the leaf characters somewhat resembling those of *L. nitidum* of Hooker, which is confined to Tasmania, but easily separated from that species, which has smaller fruits, always 5-celled. It has also some resemblance to *L. lanigerum* var. *macrocarpum* Maiden and Betche, but this

latter has exceptionally large fruits, also constantly 5-celled. *L. sphaerocarpum* was originally collected at Caboon, 7 miles north of Rylstone, by Mr. R. T. Baker in October, 1893. It has since been collected in the same neighbourhood by E. Cheel, and at Cox's Creek, near Rylstone, by W. Dunn. Also at Capertee, Rocky Glen, Coonabarabran, Warrumbungle Ranges, Clarence Siding, Hartley Vale, Mount Wilson, Mount Victoria, and Blackheath.

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NOTES ON WATTLE BARKS.
Part III.

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Introduction.

Some years ago, an investigation was commenced of the tanning value of certain New South Wales Wattles belonging to the so-called *Acacia decurrens* group. Botanical material was collected, together with bark samples, in order to determine whether the various members of this group could be easily recognised. Another object of the investigation was to determine whether, by the establishment of small plantations from seed obtained from trees which had been proved to yield a bark with high tannin content, it would be possible to improve the average tannin yield from locally grown wattles. Unfortunately, the necessary assistance to carry out this project was not made available, and pressure of other work has so far prevented the fulfilment of the scheme. From an examination of the analytical figures given for the barks of *Acacia mollissima*, it is very evident that New South Wales possesses excellent potential parent trees.

It has been generally recognised that *Acacia mollissima* yields the best tan bark of this group, and therefore especial attention was devoted to the analysis of a number of barks from different localities to determine whether the high yield was generally consistent.

The *Acacia decurrens* group was regarded by Maiden[1] as containing the following principal varieties: (a) var. *normalis* Benth., now described as *A. decurrens* Willd.; (b) var. *mollis* Lindl., now *A. mollissima* Willd., (c) var. *pauciglandulosa,* F.v.M., now *A. irrorata,* Sieber; (d) var. *Leichhardtii,* Benth., now *A. Arundelliana,* Bailey; (e) var. *dealbata,* F.v.M., now *A. dealbata* Link, and in addition there is another species, *A. filicifolia,* Cheel and Welch. There also appears to be a very definite form occurring over a fairly wide area which can best be regarded as a variety of *A. mollissima,* but further data is required. The "decurrens" group has in common, wattles with feathery bipinnate leaves, which are decurrent on the stems, and flowers arranged in heads.

After a careful examination of a large amount of botanical material, there does not appear to be any doubt but that these species are well established, and can be easily differentiated, and that the limits of variation are such that there need be no confusion between them.

In the following descriptions, only general and leaf characters are given. Floral characters have not been detailed, since wattles are only in flower for a short period during the year, and it is important to be able to separate the species when flowers are absent. A key to the identification of the species is given at the end of the paper.

Bark Analyses.

The results given under bark analyses are from butt samples, and can be regarded as the maximum for the tree, since, in general, tannin content varies directly as bark thickness. All analyses have been corrected to a standard moisture content of 11.5%, the "insolubles" being obtained by subtracting the sum of the tannin, soluble non-tannins and water, from 100.

The bark thickness is that obtained by measurement of the air-dry bark, and has been given with the analyses, since it must be regarded as an important factor. At the same time, exceptions undoubtedly occur which may be due to other influences, such as rate of growth and its relation to the proportion of old cells in the bark, and possibly physiological variations in the individual tree. This is referred to in our earlier work.[2]

The major works on wattle barks, generally, are those of Maiden[3] and, later, Coghill[4]. These are referred to under the various species, but attention should also be drawn to the analyses made by Blockey[5] of samples sent by Maiden to the Yorkshire College. According to these results, *A. mollissima* showed a lower tannin content than *decurrens* (*normalis*) *or Arundelliana* (*Leichhardtii*), and is little better than *irrorata* (*pauciglandulosa*). The results are based on single samples, which might not be representative.

Wind[6] gives analyses of barks from young trees (two-three years) grown in the Dutch East Indies, including the *A. decurrens, var. normalis, dealbata, mollissima* and *pauciglandulosa; mollissima* and *pauciglandulosa* are grouped together, and the tannin content varies from 20.46—24.33%.

Many analyses of Acacia barks cultivated abroad are also tabulated in the valuable bulletins of the Imperial Institute.[7]

Dekker[8] tabulates a number of analyses, chiefly based on Maiden, Blockey, and Zimmerman.

A very complete investigation has been made by Williams[9] of the bark of *A. mollissima,* grown in South Africa. This species has undoubtedly proved its worth under cultivation.

Chauvel[10] gives the tannin content of bark samples from four and six-year old trees of *A. mollissima,* grown in Madagascar, as 43.5 and 35.2%, respectively, and of *A. dealbata* as 23.8%.

Shinn[11] gives tannin values of A. decurrens, A. mollissima and *A. pycnantha,* grown in California, as 42.5, 46.0 and 41.8%, respectively, and states "that the superior value of *A. decurrens mollis* (i.e., *A. mollissima*) is plain."

Additional references are to be found in our earlier work.

Acacia decurrens, Willdenow[12] (*A. decurrens* var. *normalis,* Bentham).

Black Wattle.

This is evidently the species referred to by Bentham[13] as var. *normalis,* although he describes the leaflets as long and narrow, usually 3-4 lines (5-7 mm.), whereas usually they are at least 10 mm. in length. Maiden[1] followed Bentham in regarding this species as var. *normalis.* It is very distinct from the other species, and the variety has been dropped.

Description: A medium-sized tree, reaching a height of 40 feet and 15 ins. in diameter; bark usually smooth.

Leaves and branchlets tomentose when young, becoming almost glabrous or lightly sprinkled with hairs. Leaves very decurrent with prominent angles on the branchlets; up to 200 mm. in length.

Pinnae, opposite; 5-12 pairs; up to 80 mm. in length.

Glands prominent, usually one at the base of each pair of pinnae, or, rarely, an additional one on rhachis below junction of pinnae.

Pinnules widely spaced, often with an interval equal to four times the width of the pinnule between each; alternate

or opposite; narrow linear, inclined to become semi-terete; 8-18 mm. in length, usually about 10 mm.; ½-1 mm. in width; occasionally leaves with flat pinnules up to 1½ mm. in width may occur together with more linear leaves on the same branchlet.

Flowering period about August. Pods ripen in about six months.

Range: Chiefly confined to moderately high elevations, e.g., Bargo, Thirlmere, Moss Vale and Marulan districts. Does not appear to occur on the coast or at high elevations, except under cultivation.

TANNIN ANALYSES.

Moisture 11.5%

Bark Thickness (mm.)	Tannin	Non-Tannin	Locality
6–7	45.4	9.6	Bargo
5	45.2	10.0	Bargo
3	44.5	10.6	Bargo
5–6	43.3	10.6	Bargo
5	41.9	11.6	Bargo
3	40.3	11.8	Bargo
8	39.5	9.9	Bargo
5	36.0	13.5	Bargo

Maiden[3] gives the results of only two barks which, if analysed by modern methods, would probably give figures comparable with those now obtained. Coghill[4] gives two analyses from Victorian grown trees, and one from Gosford, N.S.W., the results being in the vicinity of 40% tannin; these barks are evidently from cultivated trees, since *A. decurrens* does not occur in these localities.

The results of our analyses show that *A. decurrens* ranks close to *A. mollissima*, and must be regarded as

yielding a useful bark. Further work is necessary to determine whether the yield of bark may be greater than that of *A. mollissima* under certain conditions.

ACACIA MOLLISSIMA, Willdenow[14] (*A. decurrens* var. *mollis*, Lindley[15]).

BLACK OR GREEN WATTLE.

This species, which was first described by Willdenow in 1809, was regarded as variety *mollis* of *A. decurrens* by Bentham[13], and Maiden[1] supported this view since, in his opinion, the other varieties of *A. decurrens* passed by gradation, one into another. Mueller[16] gave it specific rank. The economic importance of this species, together with the fact that it can be readily recognised in the field, or as herbarium material, has resulted in Willdenow's name being now almost universally adopted.

A large collection of botanical and bark specimens has been made from New South Wales, and through the courtesy of the various Forestry Departments, material was also obtained from trees grown in Victoria, New Zealand and South Africa. A comparison has also been made with herbarium specimens from Tasmania, and there does not appear to be any doubt but that the mainland and Tasmanian material are specifically identical.

Description: A medium-sized tree, up to 45 feet in height, and 18 ins. in diameter. Bark usually smooth, dark brown in colour, occasionally in old or diseased trees showing ross.

Leaves and branchlets densely tomentose when young, and golden yellow in colour, older leaves and branchlets becoming more glabrous, until they may be only covered with scattered hairs, the upper surfaces of the leaves

practically glabrous. Branchlets occasionally slightly glaucous.

Pinnae usually opposite, occasionally both opposite and alternate in the same leaf; broad linear in outline; 6-20 pairs, rarely less than 8; 20-60 mm. in length, usually about 45 mm.

Glands, 1-4 on the rhachis between each pair of pinnae, occasionally almost entirely solitary and rounded, but varying from 1-3 in the same leaf; where crowded, they are often elongated and confluent. Secondary glands very rarely present on the bases of the pinnae.

Pinnules crowded, occasionally overlapping, more rarely spaced so that the gap may exceed the width of the pinnule; usually alternate; spathulate to linear-oblong; usually obtuse, rounded or truncate, sometimes shortly acute; angle of attachment varying from 45°-90°; usually 3-5 mm. in length; 0.5-0.75 mm. in width.

Flowering period, October to December, usually November. Pods do not ripen for about 12 months.[17] Pods inclined to be rough, usually contracted between seeds.

Range: In New South Wales, it reaches its maximum development on the South Coast, below Nowra, especially in the Eden district. It is also common on the southern highlands in the Bowral-Mittagong area. It is not common north of Sydney. A more glaucous form is found in the Blue Mountains and Sydney districts. It does not occur at high elevations, nor does it seem to occur west of the Dividing Range. It is common in Victoria and Tasmania, but it is doubtful whether it occurs in Queensland. In N.S.W. it generally prefers well-drained slopes and is not commonly found near water.

TANNIN ANALYSES.

Moisture 11.5%

Bark Thickness (mm.)	Tannin	Non-Tannin	Locality
10	53.5	8.3	Pericoe
3-4	51.9	9.1	Kangaroo Valley
7-8	49.8	8.8	Eden
7-8	49.6	9.2	Lal Lal, Victoria
6	49.4	11.1	Falls Creek
6-7	48.9	9.0	Pericoe
7	48.4	7.1	Kangaroo Valley
6	48.4	8.5	Falls Creek
5-6	48.1	9.2	Pericoe
6-7	47.9	9.1	Pericoe
5-6	47.8	7.5	Pericoe
6	47.6	9.5	Cedara, Natal
—	47.6	8.9	Falls Creek
5-6	46.5	8.8	Nilgiris, India
7	46.3	11.8	Falls Creek
5-6	46.2	8.5	Eden
5	46.0	9.8	Pericoe
5-6	45.8	10.2	Nowra
3-4	45.6	9.5	Lal Lal, Victoria
4-5	45.5	9.6	Nowra
4-5	45-3	10.5	Bowral-Mittagong
7-8	45.0	8.9	Rotorua, N.Z.
6	44.9	8.1	Pericoe
5	44.8	8.9	Fitzroy Falls-Bowral
4-5	44.0	7.3	Eden
3-4	43.9	7.8	Nowra
3-4	43.9	10.5	Nowra
3-4	43.9	10.8	Bowral-Mittagong.
5-6	43.8	9.9	Pericoe
5-6	43.8	8.0	Cedara, Sth. Africa
8-9	43.6	8.1	Eden

Bark Thickness (mm.)	Tannin	Non-Tannin	Locality
3-4	43.5	9.9	Delatite, Victoria.
4-5	43.5	9.9	Mt. Cole, Victoria
4-5	43.3	9.2	Nowra
5.	43.0	11.5	Delatite, Victoria
5-6	42.7	10.6	Pericoe
5	42.7	8.3	Cedara, Sth. Africa
—	41.7	7.4	Moruya
4-5	40.2	7.8	Eden
4-5	40.2	10.1	Bateman's Bay
4-5	39.0	12.6	Sth. Africa
2-3	38.8	7.8	Bateman's Bay.
5	37.5	11.5	Rotorua, N.Z.
6-7	37.5	6.8	Pericoe
2-3	35.4	10.7	Bateman's Bay
5-6	34.6	8.1	Pericoe
3-4	32.9	10.0	Bateman's Bay
5	28.1	6.6	Mt. Cole, Victoria

Maiden[3] gives figures for *A. mollissima* analysed by the old Lowenthal Method. One analysis shows 69.33% extract, 36.4% tannin; analysed by modern methods such a figure for extract or total solubles would give at least 50% tannin.

Coghill[4] gives the results of analyses from Queensland, N.S.W., Victoria and Tasmania. Only one analysis is given for a N.S.W. sample, and this shows 22.8% tannin from a Gosford tree. It is very doubtful whether *A. mollissima* occurs naturally in the Gosford district, and from this analysis, compared with our results, it appears doubtful whether the identification is correct. The Queensland sample from Imbil (Coghill[4]) 27.2%, unless cultivated, is also doubtful. Cultivation in South Africa, British East Africa, India, New Zealand and elsewhere, has shown prac-

tically without exception that this species produces a bark with a high tannin content, and this is confirmed by our analyses not only of local barks, but also of samples from New Zealand, India and South Africa.

Taking into consideration bark thickness, the following results are obtained:—

Bark Thickness (mm.)	Tannin	No. of Samples
2-3	37.1	2
3-4	43.7	7
4-5	42.6	8
5-6	42.7	15
5-6	42.7	5
6-7	46.4	7
7-8	47.8	5
8-9	43.6	1
9-10	53.5	1

These show a gradual increase in tannin content corresponding to an increase in bark thickness, with one exception, namely 8-9 mm., which represents, however, only one sample. There appears to be ample justification for the belief of the tanner that ''heavy'' bark gives the best results. In an examination of the actual analyses, however, it is interesting to note that the second highest result, namely 51.9% tannin, was obtained from a comparatively thin bark, and as already mentioned, there is more in the problem than bark thickness alone when dealing with individual trees.

Of the samples analysed two gave over 50%, 38 over 40%, 7 over 30% and one under 30% tannin.

The remarkable tannin content of 53.5% obtained from a sample of *A. mollissima* places it well on a level with the highest figures obtainable from *A. pycnantha.*

Proctor[18] gives analyses of three samples of *A. mollissima* supplied to him by Maiden, with tannin varying from 36-41%, and records 40-50% for *A. pycnantha*. Proctor's figures for *A. mollissima* may be legitimate for bulk samples but they should not be compared with what are evidently analyses of picked samples of *A. pycnantha*, since in our opinion the relative value of the two barks is by no means in this ratio. Bennett[19] gives a figure of only 36% tannin for *A. mollissima*.

It is desirable that attention should be drawn to the fact that butt samples of *A. mollissima* bark can also be found to give tannin results of 50% or more and it is apparent that justice has not been done to this wattle.

The apparent inferiority of the bark has been no doubt largely due to the close resemblance, in the eyes of the layman, of the tree to others which possess barks of definitely lower tannin content, and this is probably the reason why "South Coast" bark is regarded by tanners as being inferior to "Adelaide" bark (*A. pycnantha*). Provided *A. mollissima* is kept distinct there seems to be little reason why this inferiority should exist.

Acacia irrorata, Sieber[20], (*A. pauciglandulosa*, F.v.M.)

Green Wattle or Blue Skin.

A. irrorata was placed by Bentham[13] under *A. dealbata*, the locality given being Port Jackson and the Blue Mountains. *Acacia dealbata* does not occur in the Port Jackson district, whilst *A. pauciglandulosa* is one of the commonest feather leaved wattles both here and on the Blue Mountains. Cheel[21] has suggested that *A. irrorata* is identical with *A. pauciglandulosa*, and is of the opinion that *A. irrorata* should replace *A. pauciglandulosa*, due to the priority of Sieber's description. Without evidence to the contrary, Cheel's suggestion has been adopted.

Description: A medium sized tree up to 60 feet in height and 18 ins. in diamter, bark commonly brownish green, bright green on young trees and branches.

Young leaves and branchlets often very woolly tomentose; shoots golden yellow; hairs usually tubercular, the small tubercles causing the rhachis of the leaves and decurrent angles on the branchlets to become scabrous, a feature which readily separates this species from the others; older leaves sprinkled with hairs; length 60-160 mm., not usually exceeding 100 mm.

Pinnae usually opposite, inclined to be lanceolate in outline, usually 6-12 pairs; 25-60 mm. in length.

Glands, few in number or occasionally wanting, often only a single gland at the base of the upper pair of pinnae, occasionally a single gland at the base of each of four upper pairs of pinnae, sometimes one gland at base of lowest pair of pinnae; very rarely two glands in contact.

Pinnules, usually very crowded and overlapping—rarely slightly spaced; opposite or alternate; linear to narrow lanceolate, shortly acute or acuminate, not rounded; angle of attachment 30°-60°; not exceeding 6 mm. in length, usually 3-5 mm.; about 0.5 mm. in width.

Flowering period about December. Pods take 12 months to ripen; often somewhat constricted between seeds.

Range: *A. irrorata* prefers moist situations, and is the common form found near creeks and watercourses in the Sydney district. It extends south along the coast to beyond Narooma, but does not occur in the Eden district, nor does it occur in Victoria. North of Sydney it is very prevalent, practically replacing *A. mollissima;* it extends into Queensland.

TANNIN ANALYSES.
Moisture 11.5%.

Bark Thickness (mm.)	Tannin	Non-Tannin	Locality
3-5	35.1	9.4	Passchendaele, Q.
2-3	34.6	8.7	Nowra
3	33.4	8.6	Nowra
4	33.1	8.6	Nowra
2-4	33.0	10.5	Bundaberg, Q.
3-4	32.4	9.0	Nowra
2-3	31.9	9.2	Terrigal
2-3	31.6	8.6	Nowra
3-4	30.2	8.7	Terrigal
3	30.2	10.0	Terrigal
2	30.1	12.6	Terrigal
2-3	29.7	8.9	Terrigal
4-5	29.5	11.1	National Park
3	28.8	10.3	National Park
1-2	28.7	11.5	Cockle Creek—Cowan
4-5	28.4	9.5	National Park
1-2	28.2	11.1	Nowra
3-4	28.2	8.7	Nowra
2	27.6	10.6	Terrigal
3-4	26.6	9.4	Terrigal
4-5	26.4	8.6	National Park
3	25.8	7.6	National Park
2-3	25.5	10.1	Terrigal
4	25.3	5.2	National Park
5-6	25.3	6.2	National Park
—	24.9	12.3	Nowra
—	24.4	7.2	Gosford
—	22.6	8.1	Nowra
3-4	22.4	7.9	National Park
2	20.7	12.1	National Park
2	20.6	10.5	Nowra
—	19.9	9.8	Bateman's Bay.

Maiden[3] gives the results of three analyses, two of which show extract figures of 52 to 53%, corresponding to a tannin % rather higher than those given by our analyses. Coghill[4] gives some seven analyses of barks from Queensland and New South Wales, with results varying from 36.1% to 23.4% tannin. The results of our analyses, with a maximum of 35.1%, and a minimum of 19.9% tannin, prove conclusively that this is an inferior bark, especially when it is taken into consideration that these results are from butt samples, many being from large, well-grown trees, in order to obtain as high a tannin content as possible. The bark, even from large trees, is usually thin.

ACACIA ARUNDELLIANA, Bailey[22] (*A. decurrens* var. *Leichhardtii*, Bentham[13])

SILVER WATTLE.

This Acacia was raised to specific rank by Bailey. Mueller and Maiden[23] were also of the opinion that this was a distinct species and called it *A. O'Shanesii*, but gave no description. Apparently, Maiden[3] later allowed the name *O'Shanesii* to drop, since the variety *Leichhardtii* is restored and the statement is made that it is impossible to separate it from var. *pauciglandulosa*, since it may be looked upon as var. *pauciglandulosa* with long hairs, or var. *pauciglandulosa* is var. *Leichhardtii* with short hairs. Similar statements are made in the Forest Flora[1].

Apart from the fact that this tree yields a much superior bark to *A. irrorata* (*pauciglandulosa*), it appears to be quite distinct from that species and can readily be recognised in the field.

Description: A medium sized tree reaching a height of 45 feet and 18 ins. in diameter. According to Maiden[1], trees have been noted up to 36 ins. in diameter. Bark smooth, brownish in colour.

Leaves and branchlets very pubescent, much more so than *A. irrorata*; young shoots very golden yellow; branchlets not scabrous; foliage very dark green and not glossy. The tree can be readily separated from *A. mollissima* or *A. irrorata* in the field by this character. Older leaves almost glabrous and decidedly paler on the under surface (the only member of the group here described which shows this feature): up to 120 mm. in length. The foliage is more delicate and graceful than that of the other members of the "*decurrens* group."

Pinnae usually opposite; 7-20 pairs; 25-45 mm. in length, usually 30 mm.

Glands intermediate in number between *A. irrorata* and *A. mollissima,* e.g., they may extend for half the length of the rhachis, or more rarely may be quite wanting, sometimes one at top, one at middle and one at bottom of leaf; practically always solitary to each pair of pinnae.

Pinnules rarely crowded, usually spaced with intervals up to twice width of pinnule; opposite or alternate; linear oblong to narrow ovate; obtuse or shortly acute; angle of attachment 45°-90°; 3-5 mm. in length (Q), often not exceeding 2 mm. (N.S.W.); 0.6-1.0 mm. in width.

Flowering period about August. Pods take about 6 months to ripen; thin, often glaucous.

Range: New South Wales, chiefly confined to a coastal area of about 400 sq. miles in the Clyde River district; not occurring much south of Mogo or north of Cockwhy Creek; it prefers the beds of watercourses. It is remarkable how this species is very common in this area yet does not seem to occur elsewhere in New South Wales. The local explanation is that these trees have grown from seeds brought from Tasmania! by Ludwig Thomsen about 60 years ago. It

occurs also in Southern Queensland. Bark samples analysed were chiefly from southern New South Wales.

TANNIN ANALYSES.
Moisture 11.5%.

Bark Thickness (mm.)	Tannin	Non-Tannin	Locality
7	43.5	7.2	Bateman's Bay
5-6	40.9	7.9	Bateman's Bay
6	38.8	6.1	Bateman's Bay
7	38.8	5.3	Bateman's Bay
4-5	35.6	6.3	Bateman's Bay
2-3	32.6	8.8	Bateman's Bay
1-2	27.1	13.0	Kilkivan (Q.)

This bark is the so-called "Silver Wattle" of the South Coast.

Maiden[3] gives the results of four analyses from the South Coast. The highest tannin value being 25.25%. Brunnich and Jeffries[24] give an analysis of a Queensland sample with a tannin content of 17.46%. From our analyses it is evident that this species yields a very useful bark, and is well worthy of further investigation, although nothing is known of its sylvicultural possibilities.

ACACIA DEALBATA, Link[25].

SILVER WATTLE.

This species was separated from *A. decurrens* by Bentham[13]. Mueller, according to Bentham, regarded this as a variety, but later[16] adopted the same view as Bentham. Maiden[1] placed it as a variety of *A. decurrens,* stating that it "is an extreme form of var. *mollis.*"

Our experience has been that the bark is so inferior, that no good purpose could be served by linking it with *A. mollissima;* moreover, the morphological characters seem sufficiently distinct for Link's name to be adopted.

Description: Usually only a small tree in New South Wales, rarely exceeding 30 feet in height and 12 ins. in diameter, but recorded as reaching a large size, up to 11 feet girth and over 100 feet in height, in Tasmania. Bark in New South Wales trees often heavily rossed.

Leaves and branchlets covered with a short pubescence especially when young, becoming more glabrous with age. Young shoots often yellow, but colour usually less pronounced than in other species. The leaves and branchlets are normally pale green in colour, and appear lighter due to the white hairs; in addition, the presence of a white waxy bloom gives the tree a silvery appearance. Whilst the glaucousness of the branchlets and leaves is variable, thus one part may be quite white and another pale green and free from bloom, the general whitish appearance is very distinct from that of the other species. Leaves up to 160 mm. in length but usually much shorter.

Pinnae almost always opposite, 8-30 pairs, usually 10-20; 15-35 mm. in length.

Glands single at junction of pairs of pinnae.

Pinnules usually crowded, more rarely slightly spaced; opposite or alternate; broad linear; obtuse; angle of attachment usually about 60°; usually 2-5 mm. long and 0.6-0.75 mm. wide, rarely occasional leaflets may be 9 mm. long and up to 1 mm. wide.

Flowering period August and September. Pods take about six months to ripen.

Range: Although recorded by Bentham for Port Jackson, this does not appear to be correct, being confined to comparatively high elevations in New South Wales. It does not occur along the coastal strip. It occurs commonly in Victoria and Tasmania, and is recorded for Southern Queensland.

Tannin Analyses.

Moisture 11.5%.

Bark Thickness (mm.)	Tannin	Non-Tannin	Locality
4-5	36.6	7.0	Mt. Cole, Vic.
3-4	35.9	6.2	Delatite, Vic.
2	34.0	9.1	South Africa
4-5	32.3	8.4	Lal Lal, Vic.
4-5	31.5	6.1	Murraguldrie
3-4	30.7	8.1	South Africa
4	30.6	7.6	Mt. Cole, Vic.
3	30.0	9.9	South Africa
2-3	29.9	13.3	South Africa
2-3	29.7	8.5	Rotorua, N.Z.
2-3	28.4	9.7	Rydal
4-5	28.0	6.4	Delatite, Vic.
2-3	27.4	13.8	South Africa
2-3	26.1	9.8	Nundle
3-4	26.0	5.4	Murraguldrie
2-3	25.4	9.3	Rydal
5	24.9	7.2	Rydal
5	24.6	6.3	India
7-8	23.7	7.8	Rotorua, N.Z.
2.3	23.1	13.9	Lal Lal, Vic.
3-4	23.1	6.6	Burwood (cult.)
3-4	21.9	10.6	Nundle
5-6	21.0	8.9	Nundle
3-4	20.8	11.8	Nundle
1-2	20.5	8.1	Nundle
5-6	20.5	5.6	Rydal
3	20.3	9.2	Nundle
5-6	17.4	7.6	Nundle
2-3	16.1	8.9	Murraguldrie

A sample from Rotorua, New Zealand, with 47,6% tannin has been discarded since other trees from the same locality gave only 29.7% and 23.7% tannin. The botanical material supplied with the bark is undoubtedly *A. dealbata*. Coghill[4] records 22 analyses from Victoria and Tasmania, the highest being 32.3% and the lowest 13.9% tannin. Maiden's[3] results are also consistently low. All the evidence to date confirms the view that *A. dealbata* yields an inferior bark, and this is shown clearly by the results given above for cultivated samples from New Zealand, South Africa and India, as well as for naturally grown material from N.S.W. and Victoria. Although the flowering periods are different, it is not advisable to cultivate this wattle with *A. mollissima*.

Acacia filicifolia (Cheel and Welch[26]).

Fern-leaved Wattle.

Apparently this species was regarded as one of the connecting links between several members of the *decurrens* group, and was probably responsible for some of the confusion. It is quite distinct over the whole of the range.

Description: A medium sized tree reaching a height of 40 feet and a diameter of 18 inches. Bark smooth, brownish in colour. Leaves and branchlets tomentose, becoming more glabrous with age; branchlets often glaucous; leaves up to 170 mm. long.

Pinnae usually opposite; 5-12 pairs; up to 75 mm. in length.

Glands numerous, 2-5 to each pair of pinnae; separate or occasionally confluent; secondary glands often present, either on base of pinnae or as many as 5 distributed along its axis.

Pinnules normally crowded; occasionally some leaves may show spacing of greater width than pinnules; opposite or alternate; narrow linear, often spathulate, shortly acute; angle of attachment from 30°-60°; usually 5-7 mm. long; usually 0.5-0.75 mm. wide, occasional leaflets up to 9 mm. long and 1.5 mm. wide.

Flowering period August to September, more rarely October. Pods probably take six months to ripen; broad.

Range: It extends along the slopes of the Dividing Range from Rydal to the Queensland Border. It appears to be rare on the coast except between Nowra and Clyde River, and is very common in damp situations about Yerriyong.

TANNIN ANALYSES.

Moisture 11.5%.

Bark Thickness (mm.)	Tannin	Non-Tannin	Locality
—	31.4	8.8	Nowra
3	31.4	10.5	Nowra
1-2	30.5	7.4	Nowra
3	30.1	5.7	Nowra
1-2	29.8	9.0	Nowra
—	29.2	7.2	Nowra
2	29.1	9.3	Nowra
2	28.6	7.5	Nowra
3-4	28.5	6.1	Nowra
3	25.6	8.5	Nowra
2	24.8	8.9	Nowra

From the results of these analyses this can only be regarded as an inferior bark, but further samples are desirable from some of the northern areas in which this species occurs. It is important that this species should

be recognised as inferior and not confused with *Acacia decurrens* or *A. mollissima.*

The following key to the identification of the species is based on leaf characters.

(a) Glands never extending full length of rhachis:

- (b) Pinnules narrow, acute, crowded, glands not usually exceeding 3 in number, rhachis and young stems scabrous = *A. irrorata.*
- (b_1) Pinnules broad obtuse, usually not crowded, glands often extending half length of rhachis; not scabrous = *A. Arundelliana.*

(a_1) Glands always extending full length of rhachis.

- (c) Pinnules rarely or never exceeding 5 mm. in length.
  - (d) Leaves and stems usually glaucous = *A. dealbata.*
  - (d_1) Leaves and stems rarely glaucous = *A. mollissima.*
- (c_1) Pinnules rarely under 5 mm. in length.
  - (e) Pinnules 8-18 mm. in length widely spaced = *A. decurrens.*
  - (e_1) Pinnules 5-9 mm. long, usually crowded, never widely spaced = *A. filicifolia.*

In addition to these, there are several other allied species, e.g., *A. Jonesii,* Mueller and Maiden[23] and *A. pubescens*[27] R.Br., are both shrubs. *A. Muelleriena*[28] Maiden & Baker, is a shrub or small tree from the interior with sparse widely spaced pinnules. *A. Deanei*[29] (*A. decurrens* var. *Deanei*) Baker, is an interior shrub with a superficial re-

semblance to *A. mollissima,* but with few pairs of pinnae and coarser pinnules. *A. decurrens* var. *lanigera* Maiden[3] is an interior shrub or small tree with a densely hairy indumentum on leaves, stems and pods.

None of these is likely to be confused in the field with those species which have been described in this investigation.

Summary.

An investigation has been made of the tannin contents of the barks of the principle Acacias belonging to the so-called "decurrens" group, and botanical material has also been critically examined. Six species which can be recognised as distinct are described, and details are given of their leaf and general characters, together with the results of a number of bark analyses, which are summarised in the following table:— *(see next page.)*

In reviewing the results of the analyses dealt with in this paper, it is apparent that the species can be divided into two main groups as far as the value of their barks is concerned. Thus *A. mollissima, A. decurrens* and *A. Arundelliana* can be placed in this order of merit in the superior group, and *A. filicifolia, A. irrorata* (*pauciglandulosa*) and *A. dealbata* in the inferior group.

On the whole those species with thin barks give low tannin contents, but even with barks of similar thickness the inferior species possess lower tannin content than those belonging to the superior group.

Acacia mollissima is the outstanding species with regard to tannin content, although *A. decurrens* and *A. Arundelliana* also yield useful barks, and may prove of value under conditions which are unfavourable to *A. mollissima.*

THE FOLLOWING TABLE SUMMARISES THE RESULTS OF THE ANALYTICAL WORK.

Tannin Content of all Barks.

Bark thickness in mm.	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	9-10	Mean
A. mollissima	28.1(1)	37.1(2)	43.7(7)	42.6(8)	42.7(15)	46.4(7)	47.8(5)	43.6(1)	53.5(1)	44.0(48)
A. decurrens	—	—	42.4(2)	—	41.6(4)	45.4(1)	—	39.5(1)	—	42.0(8)
A. irrorata	28.4(2)	28.0(9)	29.6(11)	28.5(5)	25.3(1)	—	—	—	—	28.0(32)
A. Arundelliana	—	—	—	—	39.8(2)	—	40.6(2)	—	—	36.6(7)
A. dealbata	20.5(1)	26.7(9)	26.1(8)	31.8(5)	21.7(5)	—	23.7(1)	—	—	26.2(29)
A. filicifolia	30.1(2)	27.5(3)	28.9(4)	—	—	—	—	—	—	29.0(11)

(Figures in brackets represent number of samples analysed.)

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AN UNDESCRIBED SPECIES OF WATTLE. *ACACIA FILICIFOLIA.*

By E. Cheel and M. B. Welch, B.Sc., A.I.C.

(With Plates VII and VIII)

(Read before the Royal Society of New South Wales, Dec. 2, 1931.)

Frutex aut arbor 3-5 m., nonnunquam 12 m. altus, foliis pinnatis 5-10 jugis pinnarum cum 2-3 glandulis (nonnunquam 4-5) inter jugos pinnarum, glandula purva ad basin pinnarum inter jugos inferiores foliola:um, foliolis 35-45, 5-9 mm. longis, primo pubescentibus deinde giabrescentibus, floribus in racemis, legumine 8 cm. longo, 1.5 cm. lato, glauco.

Tree usually 9 to 15 feet tall, but occasionally up to 40 feet. Branches more or less slightly angular, but not winged, the young twigs as well as the rhachis rather densely tomentose, but with age becoming glabrous and quite glaucous.

Leaves pinnate with 5 to 10 pairs of pinnæ, the rhachis raised to a well-defined ridge with 2 to 3 glands between each pair of pinnæ or occasionally 4 or 5 glands sometimes becoming confluent as in *A. mollissima.* In addition to the glands between the pinnæ there is usually a smaller gland at the base of each pinnæ between the lower pair of leaflets. Leaflets numerous (usually 35-45), rather inclined to be more spreading and fern-like than the other forms of the *A. decurrens* group; at first pubescent, but glabrous with age; usually 5-7 mm. long, but occasionally up to 9 mm. long. Flowers in racemes, the individual flowers varying from 25 to 30 in each head, mostly 5-merous

Calyx, shortly lobed, ciliate; petals, almost glabrous, sparingly ciliate; pods 8 cm. long x 1.5 cm. broad, glaucous; seeds reniform, 5 x 2-3 mm.; funicle short, slender at the base, with a thickened aril.

This species has been previously mistaken as a form of *A. decurrens,* and also confused with *A. mollissima* and *A. dealbata.* It is quite distinct from *A. decurrens,* which has very prominently angled branches, and branchlets more or less winged and mostly quite glabrous. It also differs from *A. mollissima,* which has smaller leaflets and a much narrower pod, and the flowering season is during November and December, whereas *A. filicifolia* flowers during August to October. Its nearest affinity is with *A. dealbata,* but the pinnæ of *A. filicifolia* are not so silvery and less numerous, and the leaflets are longer and more glabrous with age than those of *A. dealbata.*

Distribution.—Goulburn River (R. T. Baker, 1892); Kelgoola (R. T. Baker, 1895); Mt. Baker, Corricudgy Range (R. T. Baker, 1897); Nullo Mtn., Rylstone (R. T. Baker, 1898); Armidale (C. F. Laseron, 1907); Acacia Creek (W. Dunn, Aug., 1909); Glen Innes (W. Stewart, Aug., 1910, and J. L. Boorman, March, 1917); Torrington (J. L. Boorman, October, 1911, in flower; January, 1911 and 1916, pods); Howes Mtn., Singleton (J. L. Boorman, Aug., 1913); Pheasants Creek, Glen Elgin (J. L. Boorman, Dec., 1913); Capertee (J. L. Boorman, Sept., 1915); Yerriyong (Coombs and Welch, 1923); Nowra (Coombs and Welch, 1923); Rydal (C. F. Laseron, 1924); Shallow Crossing, Clyde River (A. McKay, 1928); Guyra (E. N. McKie, 1928); Tenterfield (Whereat, no date).

In its southern distribution it is found chiefly on alluvial flats in moist positions.

Economics.—Analyses of the bark for tannin have proved disappointing with respect to bark collected from the South Coast district, and it can only be regarded as distinctively inferior to *Acacia mollissima.* The barks so far examined yield from 25-32% tannin.[1]

Reference.

[1]Welch, Coombs and McGlynn. Notes on Wattle Barks—Part III. Jour. Roy. Soc., N.S.W., 65:226 1931.

Explanation of Plates.

Plate VII.—*Acacia filicifolia*, Cheel & Welch—Flowering branch.

Plate VIII.—*Acacia filicifolia*, Cheel & Welch—Fruiting branch (Pods).

Acacia filicifolia, Cheel and Welch. (Flowering branch.)

Acacia filicifolia, Cheel and Welch. (Fruiting branch.)

NOTES ON THE SHRINKAGE OF WOOD.

By M. B. Welch, B.Sc., A.I.C.
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(Read before the Royal Society of New South Wales Dec. 2, 1931.)

Very little data is available on the amount of lateral shrinkage which occurs during the seasoning of many Australian woods, i.e., during the drying from a green to an air-dry condition.* It has long been recognised that shrinkage varies considerably in different woods, evidently due to some inherent character within the wood. For many industrial purposes it is essential that a wood should be used which shows a minimum shrinkage; in fact excessive shrinkage is to be avoided in general. Furthermore, in cutting green timber, an allowance has to be made in order that the seasoned wood should not be under size, and some idea of the amount of shrinkage is therefore necessary.

A theoretical explanation of shrinkage is that the micellae or molecular aggregates forming the cell wall are, in green wood, held apart by water films. During the process of drying, these films contract, allowing the

* Chapman gives the results of some observations made on seven Eucalypts and three Pines during his investigation of their mechanical properties.

Chapman, R. W., "The Strength of South Australian Timbers," Bull. 9, Dept. of Forestry, South Australia. 1922.

micellae to approach each other more closely with the consequent shrinkage of the wood.

In general the shrinkage parallel to the grain is extremely small, and for most purposes can be neglected. Shrinkage in a tangential direction is usually regarded as approximately twice that of radial shrinkage; the smaller radial shrinkage being possibly due to the stiffening action of the ray cells which have their long axis at right angles to the normal wood tissue.

Any figures for shrinkage must be used, however, with caution, since this property can be influenced by a number of factors. Even mean figures based on many samples only indicate general behaviour, and not necessarily that of an individual sample. The results given herewith are not based on a large number of samples, and may, or may not, indicate the average behaviour of the species. They have been obtained from a number of commercial samples and represent the actual shrinkages measured on these woods.

Shrinkage is influenced in the same wood by variation of density; thus the following average relationship has been suggested†:—Specific gravity $\times$ 17 $=$ tangential shrinkage, green to oven dry, and specific gravity $\times$ 9.5 $=$ radial shrinkage, green to oven dry, i.e., the heavier the wood the greater the shrinkage, although there are many exceptions to this rule.

Shrinkage is also influenced by the rate of drying; wood rapidly dried usually shrinks less than when allowed to dry slowly, owing to the wood, during rapid drying, being

† Relation of Shrinkage and Strength Properties of Wood to the Specific Gravity. U.S.D.A. Bull. 676, 1919.

more liable to set in an expanded condition. Again, the ratio of tangential to radial shrinkage usually decreases with an increase in density, but this again is not always constant.

Whereas shrinkage implies the normal contraction of the wood due to moisture losses, there is a further complication, in that abnormal shrinkage may be caused by the phenomenon known as "collapse" in which, due to very large tensile stresses caused by water leaving the cell cavity, the cell walls are drawn together or collapsed. Certain Eucalypts,* especially those of low density, are very liable to this defect, the wood in extreme cases becoming extensively corrugated. Where slight collapse occurs, it is practically impossible to separate it from ordinary shrinkage.

The figures given below were obtained by cutting small sections 1 inch long in the direction of the grain 4 inches wide and 1 inch thick, from wood which was obtained as soon as possible after sawing from the log, being wrapped in damp paper to minimise moisture losses. These sections were weighed and measured, and the volume determined; they were stored inside and measured weekly to the nearest .001" for periods varying from three to twelve months, the average width being taken as the mean of the maximum

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* Elliott mentions that "the additional size allowance which many millers find it necessary to make in sawing timber which is prone to collapse, commonly amounts to more than 20% over and above the allowance necessary to cover ordinary shrinkage and machining."

Elliott, C. S., "Collapse of Timber." Reprint from Journal, C.S.I.R., November, 1930.

and minimum widths after the samples had reached an equilibrium moisture condition. A similar sized sample, cut from the same board as the specimen which was air dried, was also weighed and measured etc., and dried at 102° C. for some days to constant weight and again weighed and measured. From these results the density at air dry volume and weight; density, green volume and oven dry weight; % shrinkage green to air dry; % shrinkage green to oven dry, and volumetric shrinkage, green to oven dry, has been calculated. The moisture content was determined on sections cut adjacent to the samples which were used for shrinkage tests.

In column 1, the weight per cubic foot is based on air-dry volume and weight, and is useful practically, since it is in this condition that wood is, or should be, used for most purposes. In column 2 the density is based on green volume and oven dry weight, and although such a combination is, of course, impossible in practice, the results are useful for comparative purposes, being based on less variable factors. Actually, slight variations in the moisture content of air dry wood do not appreciably affect the density, since the gain in weight due to the absorption of moisture is offset by the increase in size due to swelling. The green volume and oven dry weight (Wd/Vg) density figures have one other advantage, in enabling a determination of the weight per cubic foot of the green wood to be made, a figure which is often required in determining the weight of logs, green sawn timber, etc. Thus, if the Wd/Vg weight per cubic foot is x lbs., and the moisture content y %, then the density of the green timber is

$$\frac{(100 + y)x}{100} \text{ lbs. per cubic foot.}$$

The percentage shrinkage from a green to an air dry condition, based on the green size, is given in column 3. Column 4 gives the shrinkage from a green to an oven dry condition, and was obtained from samples which were not allowed to air season before being placed in the oven. As a result the figures are in many cases lower than would have been obtained if the wood had been previously allowed to season slowly, and accounts for certain anomalies where the oven dry shrinkage approximates to, or is less than, the air dry figure. Volumetric shrinkage given in column 5 was obtained by actual measurement of the shrinkage of small specimens from a green to oven dry condition, although it is possible to calculate this figure if the tangential and radial shrinkages are known. It serves as a basis for the comparison of the relative shrinkages of the various woods. Moisture percentages given in column 6 were obtained from sections cut as soon as possible after the arrival of the test pieces. Although those forwarding the specimens used were asked to obtain the wood when freshly cut from the green log and to wrap it in wet paper to reduce moisture losses it is evident from some of the figures that the wood had commenced to dry. Since, in general, shrinkage (not collapse) is not pronounced till the fibre saturation point in the vicinity of 30% moisture is reached, the actual effect of some moisture loss on shrinkage would not be very important, but where the moisture figures given are below this amount, i.e., 30%, the shrinkage figures are likely to be below normal. The moisture figures are of value in enabling the weight per cubic foot, wet volume and weight, to be calculated, and also in most cases giving some idea of the amount of water present in freshly sawn green timber. The last column indicates the direction in which the test pieces were sawn.

Australian Timbers.

		1	2	3	4	5	6	7
Acacia melanoxylon	Blackwood	44.3	37.7	1.4	3.3	8.0	98.6	Q.
		46.6	39.8	1.9	4.2	9.0	90.3	Q.
		44.0	40.5	3.6	6.3	7.9	100.4	B.
		35.9	32.7	3.3	5.5	8.6	114.1	B.
Ackama Muelleri	Red Corkwood	38.6	32.0	6.4	10.0	18.9	96.7	Q.
		40.3	32.0	9.6	14.3	18.8	96.8	B.
Agathis Palmerstoni	Queensland Kauri	31.2	24.8	1.6	2.9	6.5	19.5	Q.*
		29.8	25.2	2.6	4.2	16.1	63.7	Q.
Alstonia scholaris	Milkwood	25.2	20.0	1.6	3.8	8.5	88.9	Q.
		23.4	—	3.2	—	—	97.0	B.
Araucaria Cunninghamii	Hoop Pine	38.8	32.6	4.3	6.0	12.0	52.2	Q.
		35.6	26.6	2.8	3.8	11.1	122.9	Q.
		31.8	26.9	3.4	5.5	14.5	58.3	B.
		32.1	26.4	5.6	8.3	13.1	95.8	B.
Callitris glauca	Cypress Pine	39.5	33.8	2.5	4.4	10.4	52.0	Q.
		39.8	34.3	2.8	4.7	8.2	29.0	Q.
		50.2	36.6	2.9	5.0	10.3	29.6	Q.
		47.0	37.6	2.7	4.8	9.2	24.3	B.*
		44.9	37.6	3.8	5.5	10.9	41.2	B.
		46.8	36.8	3.8	5.8	11.1	46.5	B.
		41.8	36.2	3.5	5.4	10.5	47.7	B.
		43.1	34.7	3.5	5.0	9.8	33.0	B.
		43.9	36.7	3.2	5.0	10.2	35.8	B.
		42.7	35.8	3.2	5.0	9.8	63.1	B.

Cardwellia sublimis	Silky Oak	38.4	31.8	1.8	2.7	11.8	82.0	Q.
		36.1	30.6	4.7	7.3	9.6	98.3	Q.
Cedrela Toona	Cedar	26.1	22.8	3.1	5.0	7.1	110.1	B.
Ceratopetalum apetalum	Coachwood	42.3	31.7	6.2	8.9	21.3	111.6	Q.
		39.8	32.4	3.9	4.5	14.0	73.8	Q.
		35.2	27.6	5.9	10.6	16.4	106.1	B.
		41.5	34.2	8.9	12.3	19.6	103.9	B.
Cryptocarya glaucescens	Brown Beech	37.6	32.4	2.0	3.6	11.3	54.5	Q.
		29.0	26.4	2.2	2.9	10.3	125.3	Q.
		29.8	22.2	5.6	6.6	9.5	151.9	B.
		37.8	31.7	3.8	5.5	13.0	57.5	O.
Cryptocarya erythroxylon	Pigeon-berry Ash	42.5	34.2	5.4	7.5	12.5	52.5	B.
Doryphora sassafras	Sassafras	39.3	32.4	3.0	5.5	19.5	66.8	Q.
		31.6	25.9	2.6	4.3	17.0	132.9	Q.
		35.5	29.4	2.4	4.5	17.0	106.0	Q.
		33.3	26.4	7.7	11.9	15.2	135.3	B.
		41.1	32.4	8.9	10.2	15.7	104.0	B.
		30.3	25.0	7.0	10.4	14.4	151.8	B.
		39.1	32.4	6.7	9.3	16.9	52.0	B.
		41.3	32.6	8.8	13.1	18.8	101.0	B.
		35.4	29.9	6.8	10.5	15.3	62.0	B.

AUSTRALIAN TIMBERS (*continued*).

		1	2	3	4	5	6	7
Dysoxylum Fraseranum	Rosewood	45.9	37.8	1.8	4.8	10.2	82.0	Q.
		45.8	39.0	2.0	5.6	14.7	93.5	Q.
		47.9	40.8	2.7	6.6	15.5	90.1	Q.
		42.3	36.6	1.5	3.7	10.3	107.0	Q.
		47.9	40.6	4.6	8.4	13.9	63.8	B.
		41.1	35.5	3.7	7.1	11.6	111.8	B.
		45.1	36.0	3.9	6.0	11.4	86.0	B.
		47.6	40.1	4.3	8.2	14.9	91.4	B.
Endiandra Sieberi	White Corkwood	52.1	42.6	6.8	7.7	16.0	53.0	B.
		52.4	43.5	6.9	9.6	15.7	43.0	B.
Eucalyptus Andrewsi	New England Peppermint	52.6	40.6	6.1	8.1	23.0	78.3	Q.
		56.0	41.2	9.1	11.1	25.5	77.1	B.
		56.3	44.6	7.4	10.9	16.5	67.5	B.
		62.4	48.0	7.7	10.1	18.2	44.0	O.
Euc. globulus (E. bicostata)	Eurabbie	56.6	44.6	5.0	6.8	17.7	61.8	Q.
		60.3	44.2	11.8	13.4	22.0	62.0	B.
Euc. botryoides	Bangalay	58.5	43.2	6.9	10.1	26.5	63.5	Q.
		61.2	44.5	11.2	13.6	24.2	64.2	B.

Euc. crebra	Narrow-leaved Ironbark	67.9	55.1	4.8	7.1	14.5	34.9	Q.
		66.0	55.1	6.1	9.4	16.5	37.5	B.
Euc. Dalrympleana	Mountain Gum	48.8	36.4	6.1	9.5	26.7	84.7	Q.
		47.9	36.7	9.7	12.9	25.0	85.5	B.
Euc. Delegatensis	Alpine Ash	40.4	31.5	5.4	7.7	25.2	115.8	Q.
		41.1	31.8	7.3	11.1	20.1	103.9	B.
Euc. eugenioides	White Stringybark	53.6	43.5	6.4	9.3	16.8	69.0	O.
		51.6	45.6	6.0	8.7	13.7	67.5	B.
Euc. fastigata	Brown Barrel	57.4	42.5	6.0	8.5	21.0	75.4	Q.
		57.6	42.5	10.1	11.5	20.0	64.4	B.
Euc. macrorrhyncha	Red Stringybark	48.9	39.2	3.6	7.2	18.5	70.4	Q.
		50.7	39.8	4.7	9.8	17.0	63.0	Q.
		49.9	39.4	7.3	9.8	19.0	67.5	B.
		50.6	39.4	6.0	9.0	16.5	66.7	B.
Euc. maculata	Spotted Gum	58.1	42.2	5.3	7.7	15.9	49.0	Q.
		44.6	37.8	4.5	9.1	19.5	86.7	Q.
		60.3	—	5.2	—	—	39.2	Q.
		58.9	50.7	8.0	11.0	18.7	44.7	B.
		55.1	44.3	6.6	10.5	18.1	52.0	B.
		56.7	46.7	8.0	9.3	15.5	49.9	B.

AUSTRALIAN TIMBERS (*continued*).

		1	2	3	4	5	6	7
Euc. microcorys	Tallowwood	57.0	—	2.8	—	—	58.0	Q.
		56.7	—	2.8	—	—	58.0	Q.
		57.4	—	2.8	—	—	58.0	Q.
		59.3	47.4	5.4	8.0	16.5	58.3	O.
		58.9	48.1	5.1	8.0	16.8	63.0	O.
		58.9	48.4	3.3	4.8	15.0	47.8	Q.
		61.9	50.7	3.5	5.1	16.5	57.2	Q.
		61.9	50.9	5.7	8.0	17.2	50.8	O.
		63.6	51.4	4.2	5.9	15.1	51.8	O.
		64.4	51.6	6.9	9.6	15.9	35.8	B.
		62.1	51.0	4.8	7.7	13.2	44.6	B.
		64.6	54.1	6.2	9.2	15.7	51.4	B.
		62.3	50.5	6.6	10.0	19.0	51.0	B.
		62.4	48.7	8.0	10.1	16.9	53.2	B.
		60.7	48.9	7.3	10.1	17.3	58.5	B.
Euc. oreades	Mountain Ash	46.5	33.5	10.7	15.5	27.5	95.0	B.
		47.0	35.8	10.7	12.2	20.0	87.7	B.
Euc. obliqua	Messmate	52.4	43.0	8.3	10.3	21.4	66.5	O.
		54.4	41.0	8.9	11.3	22.4	69.8	B.
Euc. phellandra	Narrow-leaved Messmate	43.1	35.1	3.0	5.6	20.0	88.2	Q.
(E. Robertsoni)		43.7	35.1	7.1	12.5	18.1	87.7	B.
Euc. pilularis	Blackbutt	60.9	47.9	4.3	6.5	18.0	40.7	Q.
		57.7	45.1	5.7	9.0	20.5	51.7	Q.
		50.5	40.7	5.7	6.7	18.0	47.7	O.

		57.0	48.4	2.8	5.5	9.5	19.4	B.*
		61.9	48.9	6.4	11.0	16.9	53.7	B.
		59.6	47.3	7.4	10.9	17.0	40.0	B.
E. piperita	Peppermint	60.2	47.3	9.8	11.7	18.0	65.0	B.
		60.6	47.4	9.5	12.0	18.8	62.8	B.
Euc. polyanthemos	Red Box	68.0	55.8	3.9	5.3	13.1	40.2	Q.
		67.5	55.5	5.4	7.4	13.8	40.0	B.
Euc. punctata	Grey Gum	67.4	55.0	4.8	5.6	14.9	43.3	Q.
		69.0	55.7	6.1	7.1	14.0	35.2	B.
		69.5	56.1	5.3	6.5	11.9	35.9	B.
		69.5	—	5.2	—	—	30.5	B.
Euc. rariflora	Black Box	74.2	61.0	6.2	8.3	13.5	36.3	B.
		74.5	59.8	5.7	7.4	14.7	36.8	B.
		73.2	57.5	5.9	7.7	14.3	36.7	B.
		73.1	58.5	6.0	7.0	15.2	39.6	B.
Euc. resinifera	Red Mahogany	64.8	50.7	6.7	8.2	18.3	34.2	Q.
		63.7	51.6	5.1	6.5	13.0	32.4	Q.
		57.7	46.8	4.8	9.4	19.1	41.0	Q.
		59.9	48.4	4.9	8.0	18.2	49.4	Q.
		65.6	52.5	6.2	8.5	20.3	42.4	Q.
		53.5	44.5	3.4	5.8	13.3	58.2	Q.
		54.9	45.5	6.9	9.2	15.0	62.8	B.
		61.4	49.5	6.8	7.6	14.8	53.7	B.
		62.5	49.8	6.9	10.9	21.5	39.0	B.
		58.1	48.6	5.9	9.6	18.8	41.1	B.
		66.0	54.1	5.6	8.6	15.5	30.0	B.

AUSTRALIAN TIMBERS (*continued*).

		1	2	3	4	5	6	7
Euc. rostrata	Murray Red Gum	57.0	44.9	3.8	6.2	15.4	58.0	Q.
		56.9	44.4	4.7	6.2	15.9	59.8	Q.
		54.7	42.5	7.7	7.7	15.0	70.3	O.
		57.2	42.6	9.6	10.9	22.5	51.1	B.
		47.9	39.4	5.2	10.5	16.8	70.6	B.
Euc. saligna	Blue Gum	58.3	46.3	5.5	7.8	19.6	45.6	Q.
		57.6	46.0	5.0	7.1	20.0	54.5	Q.
		55.6	38.4	5.9	11.4	29.5	60.4	Q.
		56.9	46.5	4.8	8.1	20.8	42.2	Q.
		65.1	—	7.6	—	—	43.1	O.
		60.6	47.9	6.5	8.8	19.3	44.4	Q.
		62.5	—	5.8	—	—	33.7	B.
		49.6	39.3	6.3	10.9	19.1	54.5	B.
		57.1	43.8	12.6	15.3	22.5	63.7	B.
		59.7	46.3	7.9	11.5	18.0	51.5	B.
Euc. sideroxylon	Red Ironbark	65.5	55.6	3.4	5.3	13.4	43.7	Q.
		65.0	53.0	6.0	7.8	12.3	37.5	B.
Euc. tereticornis	Red Gum	64.3	52.5	5.4	7.6	15.0	54.5	O.
		64.3	52.9	6.3	11.5	15.3	51.3	B.
Euc. viminalis	Ribbon Gum	50.7	39.8	6.4	9.1	22.3	77.4	Q.
		60.4	43.3	12.8	13.8	21.1	72.7	Q.
Flindersia Brayleyana	Queensland Maple	38.5	31.0	3.8	5.4	15.6	23.0	Q.
		34.0	27.3	3.7	5.7	15.3	66.7	Q.
		35.0	29.2	6.0	8.2	13.5	97.7	B.

Flindersia australis	Colonial Teak	57.5	46.7	5.7	8.5	20.1	28.8	B.
Geissois Benthami	Red Carabeen	38.7	31.9	3.2	4.8	14.7	82.3	Q.
		39.3	31.1	7.6	10.2	16.1	82.8	B.
Gmelina Leichhardtii	Beech	33.8	30.2	1.1	4.5	10.3	130.0	Q.
		34.0	30.0	1.2	4.4	9.9	129.0	Q.
		32.2	27.2	5.4	6.3	8.7	97.6	B.
		33.0	28.8	6.0	7.5	7.0	113.8	B.
		36.8	32.4	3.8	3.2	7.5	75.8	B.
Litsea reticulata	Bolly Gum	28.7	24.2	4.5	5.5	10.0	109.0	B.
Orites excelsa	Prickly Ash	41.9	33.8	2.4	3.7	15.8	95.4	Q.
	Silky Oak	40.9	34.6	7.1	10.2	14.8	105.4	B.
Pittosporum undulatum	White Holly	51.6	40.5	9.8	11.1	15.7	72.2	B.
Schizomeria ovata	Crab Apple	48.2	37.8	3.3	8.5	16.3	71.1	Q.
		47.9	40.4	9.6	8.5	16.0	74.0	B.
Sloanea Woollsii	Yellow Carabeen	42.0	34.4	2.8	3.9	13.2	60.5	Q.
		40.5	32.6	6.3	8.3	11.7	58.7	B.
Stenocarpus salignus	Beefwood	52.0	48.4	2.1	4.4	16.3	67.5	Q.
		52.3	44.9	2.5	5.9	17.1	68.4	Q.
Syncarpia laurifolia	Turpentine	65.2	55.4	5.8	7.8	22.5	62.8	Q.
		59.2	42.7	6.4	8.6	21.3	75.1	Q.
		59.2	42.5	6.7	8.4	24.1	73.7	Q.
		58.1	43.2	12.4	14.5	24.2	69.3	B.
		64.5	55.4	11.1	12.9	20.6	55.4	B.
Tarrietia actinophylla	Stavewood	55.1	42.9	5.4	7.3	20.1	59.5	Q.
		49.8	39.6	9.4	11.4	16.4	60.4	B.

AUSTRALIAN TIMBERS (*continued*).

		1	2	3	4	5	6	7
Tarrietia argyrodendron	Crow's-foot Elm	52.0	39.1	6.1	7.1	13.5	88.0	O.
		49.9	40.2	5.3	6.7	11.3	44.4	O.
Tristania conferta	Brush Box	44.5	40.9	4.0	5.8	17.3	80.5	Q.
		56.1	44.1	3.5	5.4	18.7	70.4	Q.
		49.7	39.5	6.4	8.8	14.0	73.3	B.
		53.0	41.8	8.1	12.3	22.8	69.7	B.
		53.6	45.5	9.2	8.6	15.7	67.7	B.
		55.4	43.6	8.6	9.4	14.7	67.9	B.
Xanthophyllum Macintyrii	Sovereign Wood	49.9	42.3	7.3	9.4	14.4	64.1	B.

NON-AUSTRALIAN TIMBERS.

		1	2	3	4	5	6	7
Acacia sp.	Noumean Blackwood	34.6	28.8	2.3	2.9	10.7	127.4	Q.
		47.8	34.2	4.4	4.5	11.4	77.9	B.
Agathis lanceolata	Noumean Kauri	35.7	29.5	2.9	4.3	11.4	36.7	Q.
		34.9	—	3.9	—	—	65.8	B.
Azadirachta integrifolia	Calantas	32.3	27.0	1.8	3.3	8.3	20.4	Q.*
Calophyllum sp.	Solisle Cedar	37.4	—	3.8	—	—	57.3	Q.
		39.5	—	5.9	—	—	60.3	B.
Quercus crispula	Japanese Oak	43.9	35.4	3.4	4.4	16.6	77.0	Q.

Shorea sp.	Pacific Maple	26.4	24.6	2.3	4.3	13.5	85.4	Q.
		29.5	24.9	2.0	3.7	11.3	66.4	Q.
		30.5	25.5	2.1	3.9	11.2	60.5	Q.
		32.4	27.6	2.6	3.9	9.8	51.5	Q.
		30.2	24.9	3.2	5.2	12.7	61.8	O.
		25.4	22.0	5.3	8.0	12.1	61.2	B.
		33.9	28.3	4.1	7.3	11.0	51.2	B.
		31.8	26.6	5.4	9.5	12.6	72.2	B.
		34.8	29.5	4.3	6.2	9.6	53.1	B.
		34.4	29.2	3.5	5.6	9.3	57.5	B.
Terminalia gigantea	Solisle Oak	28.8	24.4	1.6	3.2	9.2	95.8	Q.
		31.2	25.8	4.3	6.1	10.3	89.3	B.

* These samples have too low a moisture content to be regarded as "green."

1 = Weight per cubic foot; air dry volume and weight.

2 = Weight per cubic foot; green volume, oven dry weight.

3 = Lateral shrinkage %—green to air dry.

4 = Lateral shrinkage %—green to oven dry.

5 = Volumetric shrinkage green to oven dry.

6 = Moisture % on dry weight.

7 = Direction of cut, Q. = Quarter or radially cut, i.e., parallel to rays.

B. = Backed off or tangentially cut, i.e., at right angles to rays.

O. = Oblique, i.e., at approximately 45° to rays.

A tolerance of 15° was permitted.

The figures given in the table are self explanatory and little comment is necessary.

Certain timbers stand out as possessing a small amount of radial shrinkage, thus Beech 1.1-1.2, Blackwood 1.4-1.9, Rosewood 1.5-2.7, Silky Oak (Cardwellia) 1.8, Brown Beech (Cryptocarya) 2.0-2.2, Beefwood 2.1-2.5 are the best examples of this. Although the shrinkage of Beech is usually regarded as negligible, this is probably due to the abnormally slow loss of moisture from this wood, since the tangential shrinkage varied from 3.8 to 6.0%, i.e., about five times the radial shrinkage. Another unusual feature of this wood is the high radial shrinkage from green to oven dry, namely, 4.5% ; in most woods the ratio of oven dry to air dry shrinkage is well below 2.

In some woods the ratio of tangential and radial shrinkage is low, e.g., in Cypress Pine the mean figures are 3.5 to 2.7 respectively. Rosewood also possesses a low tangential shrinkage which no doubt accounts for the fact that this wood can be used for turnery in a practically unseasoned condition.

Woods which possess a marked difference between the radial and tangential shrinkage are most liable to warp and cup, especially when cut obliquely or backed off, and this is seen in the case of Sassafras, where the radial shrinkage is 2.7% and the tangential shrinkage 7.7%.

High figures for tangential shrinkages of about 12% were found in Turpentine and in several Eucalypts; such figures were in most cases due to collapse.

There is not sufficient data to enable any comparisons to be made between density and shrinkage.

In conclusion, acknowledgment is due to the Forestry Commission, Sydney, and many others, for the timber samples used, and especially to Mr. F. B. Shambler, of the Technological Museum Staff, for his very able assistance during the progress of the work.

ABSTRACT OF PROCEEDINGS

OF THE

Royal Society of New South Wales.

MAY 6TH, 1931.

The Annual Meeting, being the five hundredth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 8 p.m.

Professor O. U. Vonwiller, President, in the Chair.

Seventy members and thirty visitors were present.

The reading of the General Monthly Minutes of 3rd December, 1930, was deferred to the next meeting.

The President reported that this was the first meeting in Science House, and that the Official Opening would take place on the following afternoon, when His Excellency Air Vice-Marshal Sir Philip Woolcott Game, G.B.E., K.C.B., D.S.O., would formally open the building. This would be followed by an exhibition held on all floors of the building, which would include exhibits illustrating science, engineering, architecture, surveying, astronomy, etc. This exhibition would remain open until the following Saturday mid-day.

The certificates of the following candidates were read for the first time: Warnford Moppett, biologist, Cancer Research Department, University of Sydney, and Jack Maxwell Rayner, physicist to the Department of Mines, New South Wales.

The Annual Financial Statement for the year ending 31st March, 1931, was submitted to members, and on the motion of Professor H. G. Chapman, seconded by Mr. C. A. Sussmilch, was unanimously adopted.

ROYAL SOCIETY OF NEW SOUTH WALES.

Statement of Receipts and Payments for the year ended 31st March, 1931.

GENERAL ACCOUNT.

RECEIPTS.

	£ s. d.	£ s. d.
To Balance—31st March, 1930		1186 8 0
,, Revenue—		
Subscriptions...	464 2 0	
Rents	207 12 2	
Sundry Receipts	23 6 2	
Government Subsidy	100 0 0	
Interest—		
Government Bonds & Stock ... ... and Loan...	1140 1 2	
		1935 1 6
,, Liversidge Bequest—Interest		3 0 3
,, Royal Society's Fund—Interest added ...		299 7 3
,, Loan		20000 0 0
		£23423 17 0

PAYMENTS.

	£ s. d.	£ s. d.	£ s. d.
By Administrative Expenses—			
Salaries and Wages—			
Office Salary and Accountancy Fees	291 15 0		
Assistant Librarian	48 0 0		
Caretaker	202 10 0		
		542 5 0	
Printing, Stationery, Advertising and Stamps—			
Stamps and Telegrams ...	31 6 6		
Office Sundries and Stationery	7 0 8		
Advertising	4 12 0		
Printing	67 4 3		
		110 3 5	

	£ s. d.	£ s. d.	£ s. d.
Rent, Rates, Taxes and Services—			
Rent	481 4 8		
Electric Light and Gas ...	36 12 4		
Insurance	21 11 9		
Telephone	18 15 2		
		558 3 11	
Printing and Publishing Society's Volume—			
Printing, &c.	188 7 3		
Bookbinding	46 13 9		
		235 1 0	
Library—			
Bookbinding		266 14 3	
Sundry Expenses—			
Removal Expenses	17 4 0		
Repairs	23 12 2		
Lift Attendant	47 5 0		
Bank Charges	4 12 0		
Sundries	51 8 2		
		144 1 4	
			1856 8 11
,, Interest—			
Union Bank of Australia Ltd.		0 11 6	
Royal Society's Fund		299 7 3	
Loan Fund		135 14 11	
			435 13 8
,, Furniture			402 2 6
,, Science House			12606 13 10
,, J. H. Maiden Memorial Fund ...			1 1 0
,, Loan on Mortgage—Institution of Engineers ...			4950 0 0
,, Government Bonds and Stocks ...			1176 5 0
,, Clarke Memorial Fund			11 6
,, Building Investment Loan Fund			1080 0 0
,, Balance--31st March, 1931, Union Bank of Australia Ltd.			915 0 7
			£23423 17 0

Compiled from the Books and Accounts of the Royal Society of New South Wales, and certified to be in accordance therewith.

(Sgd.) HENRY G. CHAPMAN, M.D., *Honorary Treasurer.*
(Sgd.) W. PERCIVAL MINELL, F.C.A. (Aust.), *Auditor.*

SYDNEY, 28TH APRIL, 1931.

BALANCE SHEET AS AT 31st MARCH, 1931.

LIABILITIES.

	£ s. d.	£ s. d.
Investment Fund—		
Clarke Memorial Fund	1374 1 0	
Walter Burfitt Prize Fund	593 15 9	
Investment Fund...	3757 13 3	
Liversidge Bequest	565 5 2	
		6290 15 2
On Loan		2320 0 0
Sundry Liabilities		231 8 0
Accumulated Funds		29109 13 10
		£37951 17 0

ASSETS.

	£ s. d.	£ s. d.
Cash—		
Union Bank of Australia, Ltd. ...		915 0 7
Government Bonds and Stock (Nominal Value £7350)		7073 7 5
Science House Management Committee—		
Payments to date		13270 0 0
Sundry Debtors—		
Institution of Engineers...	4950 0 0	
For Rents and Sundries	40 10 4	
For Subscriptions in arrears	528 11 0	
		5519 1 4
Library—		
Insurance Valuation	9115 10 11	
Add :—Expenditure during year ...	266 14 3	
		9382 5 2
Office Furniture—Insurance Valuation ...		1452 2 6
Pictures—Insurance Valuation		180 0 0
Microscopes—Insurance Valuation		120 0 0
Lantern—Insurance Valuation		40 0 0
		£37951 17 0

Compiled from the Books and Accounts of The Royal Society of New South Wales, and certified to be in accordance therewith.

(Sgd.) HENRY G. CHAPMAN, M.D., Honorary Treasurer.
(Sgd.) W. PERCIVAL MINELL, F.C.A. (Aust.), Auditor.

Queensland National Bank Chambers,
27 Hunter Street, Sydney, 28th April, 1931.

INVESTMENT FUND.

STATEMENT OF RECEIPTS AND PAYMENTS FOR THE YEAR ENDED 31ST MARCH, 1931.

RECEIPTS.

	£ s. d.	£ s. d.
To Balance—31st March, 1930		5988 19 2
,, Interest—		
Clarke Memorial Fund	65 9 0	
Walter Burfitt Prize Fund	28 5 0	
Liversidge Bequest	29 15 6	
Investment Fund	178 18 0	
		302 7 6
		£6291 6 8

PAYMENTS.

	£ s. d.
By Expenditure—Clarke Memorial Fund	11 6
,, Balance—31st March, 1931	6290 15 2
	£6291 6 8

On the motion of Mr. C. A. Sussmilch, seconded by Professor R. D. Watt, Mr. W. P. Minell was duly elected Auditor for the coming year.

The Annual Report of the Council was read, and on the motion of Mr. C. A. Sussmilch, seconded by Mr. A. E. Stephen, was adopted.

REPORT OF THE COUNCIL FOR THE YEAR 1930-31.

(1st May to 29th April.)

The Council regrets to report the loss by death of four ordinary members and two honorary members. Twenty-one members have resigned. On the other hand, eight ordinary members and one honorary member have been elected during the year. To-day (29th April, 1931), the roll of members stands at 307.

During the Society's year, there have been eight general monthly and ten council meetings.

Four Popular Science Lectures were given, namely:—

July 17—"The Romance of Wood," by M. B. Welch, B.Sc., A.I.C.

August 21—"Natural History Museums," by C. Anderson, M.A., D.Sc.

September 18—"The Developments in Economic Importance of Carbon Compounds," by V. M. Trikojus, B.Sc., D.Phil.

October 16—"Wool Fibre; its Nature, Character and Use," by Professor J. Douglas Stewart, B.V.Sc., M.R.C.V.S.

Meetings were held throughout the Session by the Sections of Geology and Physical Science.

The Section of Industry during the year again devoted its attention to visiting industrial establishments.

Special invitations were extended to members on the following dates: Thursday, 3rd July, 1930, Amalgamated Wireless Works at Knox Street, and the Wireless Transmitting Station at Radio Centre, Pennant Hills, and on Thursday, 16th October, 1930, to the H.M.S. "Oxley."

Eighteen papers were read at the General Monthly Meetings, and covered a wide range of subjects.

Lecturettes were given at the monthly meetings in June, July, August, September, October, November and December, by Messrs. A. R. Penfold, O. U. Vonwiller, C. A. Sussmilch, Warnford Moppett, A. R. Radcliffe-Brown, A. S. LeSouef and D. T. Sawkins, respectively.

On Thursday afternoon, 14th November, 1930, a special lecture was delivered to members of the Royal Society by Professor A. S. Mitchell of the Leander McCormick Observatory, Virginia, U.S.A., on "The Recent Eclipse."

Maiden Memorial Pavilion: The Maiden Memorial Pavilion was officially opened by the Lieutenant-Governor, Sir William Cullen, on Monday, 19th May, 1930.

Science House: The foundation stone of Science House was set by His Excellency Air Vice-Marshal Sir Philip Woolcott Game, G.B.E., K.C.B., D.S.O., Governor of New South Wales, on Tuesday, 24th June, 1930, and on the 15th January, 1931, the Royal Society of New South Wales took possession of its part of the building.

The Annual Dinner took place at the University Club, Phillip Street, Sydney, on Thursday, 23rd April (St. George's Day), 1931, when we were honoured by the presence of His Excellency Sir Philip Game, Mr. S. G. Thorp (Architect for Science House), and the presidents of the Linnean Society of New South Wales, the Institution of Engineers, Australia, and the Chamber of Manufactures.

The Council has awarded the Clarke Memorial Medal to Robin John Tillyard, M.A., D.Sc., F.R.S., F.L.S., F.E.S.

The donations to the library have been as follow: 39 volumes, 1524 parts, 29 reports, 6 maps, 1 catalogue and 6 calendars.

Government Subsidy: On the 14th August, 1930, the Society was notified by the Director for Education that the government subsidy, which for many years past had been £400 per annum, would be reduced to £200 per annum.

It was announced that the Council had awarded the Clarke Memorial Medal to Dr. R. J. Tillyard, F.R.S., and the President then made the presentation. Dr. Tillyard expressed his appreciation of the Council's action in making the award.

The President announced that the following popular science lectures would be delivered this session:—

July 16—"Oysters and Oyster Culture," by T. C. Roughley.

August 20—"The Oceanographical Work of the 'S.Y. Discovery' in the Antarctic Seas," by W. W. Ingram, M.C., M.D., Ch.B.

September 17—"The Sun," by Rev. Wm. O'Leary, S.J.

October 15—"Insect Life," by W. B. Gurney, B.Sc.

A letter was read from the Consul-General for Denmark forwarding the "Dana Medal," symbolizing the circumnavigation of the Globe by the "Dana."

The following donations were received: 513 parts, 10 volumes, 5 reports, 1 calendar, and 1 catalogue.

The President, Professor O. U. Vonwiller, then delivered his address.

There being no other nominations, the President declared the following gentlemen to be officers and council for the coming year:

President:

EDWIN CHEEL.

Vice-Presidents:

Prof. R. D. WATT, M.A., B.Sc.
Prof. L. A. COTTON, M.A., D.Sc.
Prof. J. DOUGLAS STEWART, B.V.Sc., M.R.C.V.S.
Prof. O. U. VONWILLER, B.Sc., F.Inst.P.

Hon. Treasurer:

Prof. H. G. CHAPMAN, M.D.

Hon. Secretaries:

C. A. SUSSMILCH, F.G.S.
R. J. NOBLE, M.Sc., B.Sc.Agr., Ph.D.

Members of Council:

C. ANDERSON, M.A., D.Sc.
Prof. C. E. FAWSITT, D.Sc., Ph.D.
E. C. ANDREWS, B.A., F.G.S.
JAMES NANGLE, O.B.E., F.R.A.S.

Assist.-Prof. W. R. BROWNE, D.Sc.	Prof. T. G. B. OSBORN, D.Sc., F.L.S.
R. W. CHALLINOR, F.I.C., F.C.S.	A. R. PENFOLD, F.A.C.I., F.C.S.
Prof. J. C. EARL, D.Sc., Ph.D.	M. B. WELCH, B.Sc., A.I.C.

Professor Vonwiller, the out-going President, then installed Mr. Edwin Cheel as President for the coming year, and the latter briefly returned thanks.

On the motion of Professor Fawsitt, a hearty vote of thanks was accorded to the retiring president for his valuable address.

Professor Vonwiller briefly acknowledged the compliment.

JUNE, 3RD, 1931.

The five hundred and first General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 8 p.m.

Dr. C. Anderson in the Chair.

Thirty-five members and two visitors were present.

The Minutes of the General Monthly Meeting of 3rd December, 1930, and of the Annual Meeting of 6th May, 1931, were read and confirmed.

The President nominated Mr. R. W. Challinor to preside at the Ballot Box, and members elected Messrs. H. V. Bettley-Cooke and H. G. Pyke to act as Scrutineers when the following gentlemen whose certificates had been read a second time were duly elected ordinary members of the Society: Warnford Moppett and Jack Maxwell Rayner; Thomas Ranken Lyle, K.B., C.B.E., D.Sc., F.R.S., was elected an honorary member of the Society.

The following donations were received: 409 parts, 8 volumes, 7 reports and 1 calendar.

A letter was read from the Secretary of the Old Boys' Union of the Hawkesbury Agricultural College, Richmond, in regard to a proposed memorial to the late Mr. H. W. Potts, who was Principal of the College for nineteen years.

Mr. A. B. Hector gave notice that at the next meeting he would move:—

"That in view of the confusion which exists between the meaning of the 'Logical Method' and the 'Technological Method' of investigating phenomena, that equal honour and consideration be given to both methods."

THE FOLLOWING PAPERS WERE READ:

1.—"A new Colorimetric Method for measuring the Hydrogen Ion Concentration of Natural Waters," by Daphne Goulston (communicated by Prof. H. G. Chapman).

2.—"The Splenectomy of Tadpoles," by Daphne Goulston (communicated by Prof. H. G. Chapman).

3.—"Variations of the Hydrogen Ion Concentration of Sea Water," by Daphne Goulston (communicated by Prof. H. G. Chapman).

4.—"On the Metabolism of Cold-Blooded Animals," by Daphne Goulston (communicated by Prof. H. G. Chapman).

5.—"The Mineralogy and Origin of the Natural Beach Sand Concentrates of New South Wales," by H. F. Whitworth, B.Sc. (communicated by C. A. Sussmilch).

Remarks were made by Dr. W. R. Browne, Messrs. A. R. Penfold, and H. G. Raggat.

6.—"The Celluloses of Two Water Plants," by Prof. John Campbell Earl, D.Sc., Ph.D., and Miss Thelma M. Reynolds, M.Sc.

LECTURETTE:

"The Effect of Radium upon Eggs," by Prof. H. G. Chapman, illustrated by lantern slides.

JULY 1st, 1931.

The five hundred and second General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 8 p.m.

Mr. E. Cheel, President, in the Chair.

Forty members and twelve visitors were present.

The Minutes of the preceding meeting were read and confirmed.

The certificate of the following candidate was read for the first time: Frederick William Wheatley, Director of Cranbrook School, Edgecliff.

The President announced that a popular science lecture, entitled "Oysters and Oyster Culture," would be delivered by Mr. T. C. Roughley on Thursday, 16th July, 1931, at 8 p.m.

It was also announced that the First Liversidge Research Lecture would be delivered before the Royal Society by Mr. Harry Hey, Chief Metallurgist of the Electrolytic Zinc Company of Australasia Ltd., Melbourne, in the Hall of Science House, on Thursday, 24th September, 1931, at 8 p.m.

An invitation was received from the Town Clerk of North Sydney, inviting members to the ceremony of planting trees in the new reserve at Ball's Head, on Saturday, 25th July, 1931, at 2 p.m.

The President, on behalf of the Council, gave notice of the following Motion, to be submitted at the next General Meeting:—

> Rule 9.—The annual subscription shall be £2/2/-, payable in advance, but members elected prior to December, 1879, shall be required to pay an annual subscription of £1/1/- only as heretofore.
>
> This ruling to be amended as follows:—
>
> The annual subscription shall be £2/2/-, payable in advance but members who are under 28 years of age and those elected prior to December, 1879, shall be required to pay only £1/1/- yearly.

The following donations were received: 64 parts.

THE FOLLOWING PAPER WAS READ:

"Physiography of the Bathurst District," by C. A. Sussmilch, F.G.S.

Remarks were made by Messrs. E. C. Andrews, W. R. Browne, L. A. Cotton, J. MacDonald Holmes, H. G. Raggatt, and O. U. Vonwiller.

LECTURETTE:

"Modern Chemical Views on the Structure of Substances," by Prof. C. E. Fawsitt, Ph.D. (Illustrated by lantern slides.)

AUGUST 5TH, 1931.

The five hundred and third General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 8 p.m.

Mr. E. Cheel, President, in the Chair.

Thirty members and ten visitors were present.

The Minutes of the preceding meeting were read and confirmed.

The President announced the death of Mr. David Reid, who had been elected a member in 1914.

A letter was read from the Misses Reid, expressing their appreciation of the Society's sympathy in their recent bereavement.

The President nominated Mr. M. B. Welch to preside at the Ballot Box, and members elected Dr. G. Harker and Mr. H. V. Bettley-Cooke to act as Scrutineers when the following gentleman, whose certificate had been read a second time, was duly elected an ordinary member of the Society: Frederick William Wheatley.

It was announced that a popular science lecture, entitled "The Oceanographical Work of the 'S.Y. Discovery' in the Antarctic Seas," would be delivered by Dr. W. W. Ingram, on Thursday, 20th August, 1931, at 8 p.m.

A letter was read from the Under-Secretary, Department of Agriculture, Sydney, stating that a scientific expedition is being despatched by the University of Harvard, Massachusetts, U.S.A., arriving in Sydney early in August for the purpose of gathering entomological, zoological and ornithological specimens for their Museum of Comparative Zoology. The personnel of the party being: Professor W. M. Wheeler, Mr. H. Stevens, Dr. Glover Allen, Dr. R. J. Darlington, Mr. W. E. Sheville, Dr. Ira Dixon and Mr. Ralph Ellis.

Mr. C. A. Sussmilch, on behalf of the Council, moved the alteration of Rule 9 of which notice had been given at the previous meeting, namely: That Rule 9 be altered to read as follows:—

"The annual subscription shall be Two Guineas, payable in advance, but members who are under twenty-eight years of age and those elected prior to December, 1879, shall be required to pay only One Guinea yearly."

This was seconded by Mr. A. R. Penfold, and carried unanimously. The President announced that the Resolution would be submitted for confirmation at the next Annual Meeting.

THE FOLLOWING PAPERS WERE READ:

1.—"On a specimen of Fossil Timber from the Sydney Harbour Colliery," by R. T. Baker.

2.—"Notes on Bathyliths and some of their Implications," by Assist.-Prof. W. R. Browne, D.Sc.

LECTURETTE:

"The Cultivation of the Tung Oil Tree (*Aleurites Fordii*) in Australia," by A. R. Penfold, F.C.S.

EXHIBITS:

1.—"Journal Bearings made from Australian Hardwoods," by E. G. Bishop.

2.—"Avertin," by A. B. Hector.

SEPTEMBER 2ND, 1931.

The five hundred and fourth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 8 p.m.

Mr. E. Cheel, President, in the Chair.

Thirty-three members and one visitor were present.

The Minutes of the preceding meeting were read and confirmed.

The President announced the deaths of Messrs. Robert Grant, elected a member in 1922, and Sydney Harnett Stroud, elected in 1919.

It was announced that a popular science lecture, entitled "The Sun," would be delivered by the Rev. Wm. O'Leary, on Thursday, 17th September, 1931, at 8 p.m.

It was also announced that Commemorative Addresses in connection with the Centenary of Michael Faraday's "Discovery of Electro-Magnetic Induction" would be delivered by Professors J. P. V. Madsen and O. U. Vonwiller in the Great Hall of the University of Sydney on Tuesday, 22nd September, 1931, at 8.5 p.m.

The President also announced that the First Liversidge Research Lecture, entitled "The Production of Zinc by Electrolysis of Zinc Sulphate Solutions," would be delivered by Mr. Harry Hey on Thursday, 24th September, 1931, at 8 p.m.

The following donations were received: 7 volumes, 126 parts, 3 reports, and 1 calendar.

THE FOLLOWING PAPERS WERE READ:

1.—"The amount of Hydrocyanic Acid in Sorghum and some Hybrids," by H. Finnemore, B.Sc., and C. B. Cox, B.Sc.

Remarks were made by Mr. R. W. Challinor and Professor J. Douglas Stewart.

2.—"A contribution to the Chemistry of the Fruit obtained from the White Cedar Tree (*Melia Azedarach,* Var. *Australasica* D.DC.; Syn. *Melia Australasica,* A. Juss), growing in New South Wales, with notes on its reputed toxicity," by F. R. Morrison, F.C.S., A.A.C.I., A.S.T.C., and R. Grant, F.C.S.

LECTURETTE:

"Breeding for disease resistance in Plants" (illustrated by lantern slides), by W. L. Waterhouse, M.C., D.Sc.Agr., D.I.C.

EXHIBIT:

"A note on Molecular Movement," by Mr. A. B. Hector.

OCTOBER 7TH, 1931.

The five hundred and fifth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 8 p.m.

Mr. E. Cheel, President, in the Chair.

Thirty members were present.

The Minutes of the preceding meeting were read and confirmed.

Letters were read from Mesdames R. Grant and S. H. Stroud, expressing thanks for the Society's sympathy in their recent bereavements.

The President announced that a popular science lecture, entitled ''Insect Life,'' would be delivered by Mr. W. B. Gurney on Thursday, 15th October, 1931, at 8 p.m.

The following donations were received: 108 parts, 3 volumes, 6 reports, and 1 map.

The President reminded members that a ''Walter Burfitt Prize'' would be awarded during the year 1932 and that nominations should be received early next year.

The Hon. Secretary reported that the James Clerk Maxwell Centenary was being celebrated, during this month, in London, and that the Royal Society was being

represented at the celebration by Professor Kerr Grant, of South Australia, and Dr. W. H. Love, of Sydney.

THE FOLLOWING PAPER WAS READ:

"The condensation of $\alpha\beta$-Dibromocarboxylic acids with benzene in the presence of aluminium halides," by Prof. J. C. Earl, D.Sc., Ph.D., and C. H. Wilson.

The Seventy-Fifth Anniversary of the Royal Society of New South Wales.

A series of addresses upon the early history and some of the more prominent early workers of the Society was given by the following gentlemen: Dr. H. G. Chapman, Sir Edgeworth David, Dr. J. A. Dick, Mr. James Nangle and Sir Henry Barraclough.

On the suggestion of Sir Edgeworth David, it was decided to send a letter of greeting to Mr. E. F. Pittman, one of the very old members, now resident in Victoria.

A vote of thanks to the several speakers was proposed by Professor Fawsitt and carried with acclamation.

NOVEMBER 4th, 1931.

The five hundred and sixth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 8 p.m.

Mr. E. Cheel, President, in the Chair.

Twenty members were present.

The Minutes of the preceding meeting were read and confirmed.

A letter was read from Mr. E. F. Pittman, thanking members for message of greeting.

The following donations were received: 189 parts, 6 volumes, and 4 reports.

THE FOLLOWING PAPERS WERE READ:

1.—"The Essential Oil of *Leptospermum Liversidgei* var. B. and the occurrence of Isopulegol," by A. R. Penfold, F.C.S.

Remarks were made by Professor Earl and Mr. Finnemore.

2.—"Notes on the *Pericalymmœ* section of the genus *Leptospermum* (with descriptions of three new species)," by E. Cheel.

Remarks were made by Mr. M. B. Welch.

LECTURETTE:

"Recent New Zealand Earthquakes," by C. A. Sussmilch, F.G.S.

DECEMBER 2ND, 1931.

The five hundred and seventh General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 8 p.m.

Mr. E. Cheel, President, in the Chair.

Sixteen members were present.

The Minutes of the preceding meeting were read and confirmed.

The President announced the death of Mr. William Mogford Hamlet, who was elected a member in 1877, and was President in 1899 and 1908.

The certificate of the following candidate was read for the first time: Francis Goulder, A.S.T.C., A.A.C.I., Manager of the Ever-Ready Works, Marshall Street, Surry Hills, Sydney.

The following donations were received: 312 parts, 9 volumes, 9 reports, 1 map, and 4 calendars.

Alteration to Rules to provide for the admission of Corporate Members:—

Rule VIII a.—A Partnership, Firm or Company may be admitted to corporate membership of the Society.

Application for admission shall be made according to the prescribed form of certificate for ordinary membership signed by not less than three members.

Rule VIII b.—The election of such corporate members shall be in the manner set forth for the election of ordinary members as in Rule VIII.

Rule VIII c.—The subscription for corporate membership will be five guineas per annum.

Rule VIII d.—Corporate members may nominate some member of their Firm or Staff to represent them at the meetings of the Society. Such representative, however, will not be eligible to hold office or for election as a member of council. They shall have all other privileges of ordinary members.

Considerable discussion took place, and the following suggestions were made for submission to the Council:—

(a) Moved by Mr. Jacobs and seconded by Mr. Challinor, that Rule VIIIa be modified to provide for such corporate membership be not used for advertising purposes.

(b) Moved by Professor Earl, and seconded by Mr. Penfold, that in the proposed Rule VIIId that the second sentence starting with "such representative" be eliminated and replaced by the words "Such representative to be approved by the Council."

THE FOLLOWING PAPERS WERE READ:

1.—"Notes on Wattle Barks," Part III, by M. B. Welch, B.Sc., F. A. Coombs, F.C.S., and W. H. McGlynn.

Remarks were made by Messrs. A. D. Olle and E. Cheel.

2.—"An Undescribed Species of Wattle, *Acacia filicifolia*," by E. Cheel, F.L.S., and M. B. Welch, B.Sc.

Remarks were made by Mr. M. B. Welch.

3.—"Notes on the Shrinkage of Wood," by M. B. Welch, B.Sc.

Remarks were made by Mr. E. Cheel.

LECTURETTE:

"The Story of Indigo," by Prof. J. C. Earl (Illustrated with Lantern Slides).

At the conclusion, a vote of thanks was moved by Professor Fawsitt, and carried unanimously.

At the conclusion, the President wished all the members the Compliments of the Season.

ABSTRACT OF THE PROCEEDINGS

OF THE

GEOLOGICAL SECTION.

Annual Meeting, April 17th, 1931.

Mr. C. A. Sussmilch was in the Chair.

Eleven members and eight visitors were present.

Mr. C. A. Sussmilch was elected Chairman and Mr. H. G. Raggatt, Hon. Secretary for the year.

It was agreed that the night of meeting should be the third Friday of each month, and that the time of meeting should be 7.15 p.m. instead of 7.45 p.m.

EXHIBITS:

1. By Mr. W. S. Dun--A suite of Carboniferous fossils from the head of Maule's Creek, 24 miles north-east from Boggabri, including corals of the lithostrotion type and a number of brachiopods, gasteropods, and crinoids.
2. By Professor W. R. Browne—(a) Graptolites from the Upper Ordovician slates to the south of Cooma, lying on the strike of the Cooma Schists. *Diplograptus bicornis* was recognised. (b) Micaceous hematite from a schistose porphyry occurring in veins oblique to the schistosity.
3. By Sir Edgeworth David on behalf of Mr. Tom Dibley—Fossil plants, including *Thinnfeldia narrabeenensis* from the Narrabeen Shales, north of Narrabeen.

4. By Professor Cotton—A large specimen of *Clepsydropsis* from the Parish of Taree.
5. By Miss Ida A. Brown—(a) Dyke rock from Narooma, containing very large phenocrysts of hornblende, labradorite and biotite. (b) Spherulites from a quartz porphyry near Eden, with banded chalcedony.

Mr. T. Hodge Smith gave an account of his geological observations while on a recent expedition to Central Australia.

The mesas of the Tarlton Range were described and mention made of the Jervois Range area. The latter range forms a striking escarpment, suggestive of faulting and flanks a plateau about 2000 feet above sea-level. The range consists of a typical Pre-Cambrian complex, resembling the Broken Hill area. A number of minerals were collected, including a very rare type, sphærocobaltine.

At Oorobbra gneissic granite is found associated with the schist series and in the Hart Range both schist and gneiss are intersected by basic and acid intrusives.

Sir Edgeworth David, Professor Browne and Mr. Kenny discussed the address, and Mr. T. Hodge-Smith replied to points raised in the discussion.

May 15th, 1931.

Mr. C. A. Sussmilch was in the Chair.

Ten members and nine visitors were present.

EXHIBITS:

1. By Mr. E. J. Kenny, which were described by Mr. W. S. Dun, as follows—(a) Tertiary forms from South Ita and Buckalow bores; *Trigonia semi-undulata, Magasella, Corbula, Pectunculus, Turritella,* 2 spp., and a number of sharks' teeth. (b) Cretaceous forms from Tibooburra, including *Modiola eyrensis, Maccoyella barklyi, Fissilunula clarkei.* (c) Jurassic plant remains from Tibooburra; *Taeniopteris spathulatum* and *Taxites.*

Mr. E. J. Kenny addressed the section on "Some Aspects of the Geology of the West Darling District."

The distribution, lithology, structure and geological age of each major group of rocks occurring in this very wide area of 34,000 square miles were referred to, particular attention being given to the Jurassic and Cretaceous beds as exposed in the Tibooburra and White Cliffs districts. The important discovery of fossil plants of Jurassic age and of marine fossils of Lower Cretaceous age was mentioned and special reference was also made to the widespread distribution of glacial erratics in rocks of Lower Cretaceous age, which occupy a large proportion of the West Darling area.

The distribution of Tertiary marine rocks southwards from the Barrier Ranges was discussed. Information concerning these had been obtained from bore cores in which shells and sharks' teeth of Miocene (Janjukian age) had been noted. Leaves of a dicotyledonous plant, also probably of Tertiary age, were referred to as occurring in the siliceous capping of the Cretaceous rocks at White Cliffs.

Professor Cotton expressed the thanks of the meeting to Mr. Kenny for his instructive address concerning a little known area, in which the conditions for geological work are particularly difficult.

June 19th, 1931.

Mr. C. A. Sussmilch occupied the Chair.

Thirteen members and eleven visitors were present.

EXHIBITS:

1. By Professor W. R. Browne, on behalf of Miss Dunnicliff—Amygdaloidal lavas and zeolites, with fossil wood enclosed in lava, from Coonabarabran. (Stated by Mr. Kenny to belong to the Garrawilla series of Jurassic age.)
2. By Mr. M. Morrison—Beryl crystals from Thackeringa.
3. By Mr. L. L. Waterhouse—Suite of fossiliferous limestones from Colo Creek, Capertee. The fossils included

Receptaculites, *Loxonema* and *Stromatopora*. Age: Middle Devonian.

Miss Ida A. Brown addressed the section on "The Devonian sequence on the South Coast of New South Wales, and its correlation with other occurrences in South Eastern Australia."

The sequence referred to was studied on the South Coast of New South Wales between the Shoalhaven River and the Victorian border. The Devonian rocks here rest with marked unconformity on highly-folded pre-Devonian sediments.

It was pointed out that three divisions of the Devonian Rocks may be recognised as follows:—

i.—A lower series of volcanic rocks—porphyries, quartz prophyrites and tuffs.

ii.—A series of freshwater or estuarine beds containing Upper Devonian plant remains with interbedded rhyolites, felsite and basalts.

iii.—An upper series of conglomerates, grits, sandstones and quartzites containing typical Upper Devonian fossils.

The three series are separated from each other by erosional breaks, and the upper (marine) are more widely distributed than and overlap the older series.

Tentative correlations with Devonian rocks of similar type in other parts of South-Eastern Australia were suggested, reference being made particularly to the Gippsland area in Victoria.

The palaêogeography of the Devonian was also briefly considered.

Discussion followed, which was contributed to by Sir Edgeworth David, Messrs. Andrews, Sussmilch and Dun, Professors Cotton, Browne and McDonald Holmes, and by Messrs. Waterhouse, Naylor and Raggatt.

July 17th, 1931.

Mr. C. A. Sussmilch occupied the Chair.

Eleven members and eight visitors were present.

EXHIBITS:

1. By Mr. E. K. F. Naylor—Fossil flower from Tertiary beds at Bundanoon, probably *Leptospermum.*
2. By Mr. L. L. Waterhouse—(a) From Cranky's Falls, near Fitzroy Falls. Hematite concretion, polished by attrition, apparently due to its being turned round by impact of drops of water from above. (b) Chlorite in stanniferous quartz crystals from Torrington.
3. By Mr. H. F. Whitworth—Concretions of iron pyrites, surrounded by limonite from Triassic rocks, Wilde's Meadow, Moss Vale. These suggest a mode of origin for similar limonite concretions found in the Sydney District.

Professor W. R. Browne addressed the section, his subject being "Notes on the Physiography of the Upper Murrumbidgee."

The course of the Upper Murrumbidgee was described, together with those of its tributaries. In particular valley-in-valley structure was mentioned, there being well marked terraces or gravels at heights above the present river level of 50-60, 140-150, 240-250 and 400 feet. In contradistinction to the youthful tributaries which join the main stream on the left bank as far down as Tharwa, the Umaralla River, which joins it on the right bank, is mature and its tributaries occupy mature basalt-filled valleys.

At Michelago it was noted that the "valley" of the Upper Murrumbidgee is eight miles wide, the Tinderry Range forming the true eastern side of the valley. The carving out of this valley has been mainly the work of tributaries and not of the Murrumbidgee itself. It was pointed out that from Umaralla northwards the course of the Murrumbidgee is confined on the western side by the eastern boundary of a granite bathylith, and on the eastern side by bars of porphyry such as form the high ground on the east side of the river near Michelago.

The lecturer considered that the evolution of the present stream pattern had thus been determined by erosion of rocks of differential hardness and not by faulting. It was also shown that the difference in the levels of the basalt near

Umaralla was due, not to faulting, but to difference in levels in the old topography upon which they rested.

The address was discussed by Sir Edgeworth David, Mr. E. C. Andrews and Mr. C. A. Sussmilch, Professor Browne briefly replying to points raised in discussion.

August 21st, 1931.

Mr. C. A. Sussmilch was in the Chair.

Seven members and two visitors were present.

EXHIBITS:

1. By Mr. W. S. Dun on behalf of Mr. Carey—Specimens of fossil plants from Turrimetta Head. The specimens included plants which Dr. A. B. Walkom considered probably belonged to the genus *Todites*, both fertile and sterile examples being present. This constitutes the first record of the genus from the Narrabeen Series. Similar examples with somewhat larger pinnules have been recorded from the Esk Series in Queensland. At Turrimetta Head, the *Todites* is associated with *Thinnfeldia* and *Neocalamites*.

Dr. Anderson addressed the section on "The Ancestors of Man."

The subject was introduced by an outline of the orthodox view of man's line of ascent. The following types of early man were then discussed, reference being made to casts, skulls and other illustrations:—

1.—Neanderthal man (*H. Neanderthalensis*) of whom the first representative was found at Gibraltar in 1848. The type specimen was found in Neanderthal in 1857. Neanderthal man dates frcm about the time of the Riss ice stage.

2.—Heidelberg man. Considered by some research workers to be a robust example of *H. Neanderthalensis*.

3.—Rhodesian man, found in 1921. The skull found shows him to have been a very robust type of Neanderthal man.

4.—Piltdown man, found in 1927. The remains show a fairly high organisation as to head, but with an ape-like lower jaw.

Some doubt has been expressed as to their being part of the one specimen. Piltdown man belonged to the early Pleistocene.

5.—Java man (*Pithecantropus erectus*), of early Piliocene age had an ape-like skull cap and teeth, but probably had the rudiments of speech and appears to be quite entitled to admission to the genus Homo.

6.—Peking man (*Sinenthropis Pekingensis*). A skull cap was found in 1929 and the remains of twelve individuals later.

Mention was also made of the Talgai skull found in a gravel bed in a tributary of the Condamine River. The skull represents an early Australian type different from the modern aborigine.

The address was concluded by reference to other views of man's ancestry, such as those held by Wood-Jones, Tate-Regan and Osborn.

A general discussion centred about the principal exhibits referred to in the address, Dr. Anderson replying to the many questions asked of him.

September 18th, 1931.

Mr. C. A. Sussmilch was in the Chair.

Seven members and seven visitors were present.

EXHIBITS:

1. By Sir Edgeworth David—(a) On behalf of Captain A. C. Morris, laterite from the Gosford District, used as a road material. (b) On behalf of Misses Powell and Culey: specimens from gravel beds at Tuggerah Lakes identical with pebbles from Emu Plains, suggesting deposition by the same stream, an ancestor of the Hawkesbury River.

2. By Mr. M. Morrison—(a) A full section of a "kerosene" shale seam at Coolaway Mountain, (b) Wallaby excrement from Coonabarabran, (c) Tungsten ore (Scheelite, wolfram, iron and copper pyrites, bismuthinite.) (d) Ore from St. Aignan's mine, Lucknow, showing free gold. (e) Free gold enclosed in arsenical pyrites from Nelligen. (f) Epidote in quartz from

Crudine, near Sofala. (g) Quartz veins in granite from Boonoo Boonoo. (h) Graphite schist from Eyre's Peninsular, South Australia, now being worked for graphite. (i) Pencil-like piece of fibrous gypsum obtained from a locality 50 miles from Bourke. (j) Stichtite.

3. By Professor W. R. Browne—(a) On behalf of Mr. Carey from near Colinton: silicified phyllite. (b) From the Cooma-Colinton Ordovician rocks—a series of specimens showing structure; (i) sheared tuff or porphyroid rock showing puckering; (ii) puckered silicified limestone; (iii) schist showing relationship of bedding, folding and schistosity; (iv) silicified and banded chert-like rocks; (v) granitised mica schist, showing mullion structure.

Lantern slides were also exhibited in explanation of the exhibits and of the physiography of the region.

4. By Mr. W. S. Dun—(a) Specimen of *Isotelus gigas* from the Trenton of New York. (b) Specimens from Mudgee, collected by H. E. Barton, closely allied to *Mitchelldeania? Cribriformis,* Eth. fil. from Belubula and from Copper Hill, near Molong. They are probably more closely allied to the lime-secreting thallophytes than to the cœlenterates. (c) On behalf of the Australian Museum. Silicified *Cyathophyllum* and *Favosites* from Colinton.

5. By Mr. C. A. Sussmilch—A series of specimens illustrating a sequence near Kandos of about 5,000 feet of strata, mainly referable to the Devonian. (?) Mr. Dun, in discussion, mentioned that there were no fossil types present in common with those of the Tamworth Area.

6. By Mr. H. G. Raggatt—Two pieces of bore core, showing miniature dyke and sill, from the Greta series at Muswellbrook.

October 16th, 1931.

Mr. C. A. Sussmilch occupied the Chair.

Eight members and four visitors were present.

EXHIBITS:

1. By Mr. W. S. Dun—A new Ammonoid, collected by Mr. Duniface, manager of Pelton Colliery, from the Upper Marine Series at Pelton. The specimen is an almost complete one, showing portion of the body chamber and well preserved septum and suture lines. It appears to represent a new member of the Glyphioceratidæ with 7 lobes as compared with *Paralegoceras* 11, *Agathiceras* 13 and *Schistoceras* 15. There is no close resemblance to any of the Timor Permian genera.

2. By Mr. H. O. Fletcher—on behalf of the Australian Museum, *Thinnfeldia* from Bronte.

3. By Miss Ida A. Brown—Specimens of limestone from Portland, coralline and highly altered, of Silurian age.

4. By Mr. T. Hodge-Smith—On behalf of the Australian Museum; *Billitonites* from the Philippines.

Mr. H. O. Fletcher, delivered a lantern lecture on Sir Douglas Mawson's recent Antarctic expeditions, dealing more particularly with the geological aspect. Sir Edgeworth David, Professor W. R. Browne and Mr. C. A. Sussmilch contributed to a discussion of the lecture.

November 20th, 1931.

Mr. C. A. Sussmilch was in the Chair.

There were ten members and five visitors present.

EXHIBITS:

By Mr. L. L. Waterhouse—A plane table constructed by Mr. G. Watts at a very small cost, and very efficient.

The recently issued paper by T. W. E. David and C. A. Sussmilch on "Upper Palaeozoic Glaciations of Australia," (Bull. Geol. Soc. America, Vol. 42, pp. 481-522, 1931), was read in brief by the authors and discussed by the meeting. Professors Cotton and Browne and Messrs. E. C. Andrews and W. S. Dun contributed to the discussion.

ABSTRACT OF THE PROCEEDINGS

OF THE

SECTION OF INDUSTRY.

Officers: *Chairman*, A. D. Olle, F.C.S.; *Honorary Secretary*, H. V. Bettley-Cooke.

During the year the following works were visited by the members:—

May 12th.—Engineering Department, Garden Island.

June 9th.—The Globe Worsted Mills, Marrickville.

July 14th.—Australian Paper Mills, Matraville.

August 11th.—The Bunnerong Power Station.

September 8th.—The Cancer Research Department, University of Sydney.

October 20th.—Kellogg (Aust.) Pty. Ltd., Botany.

November 10th.—Toohey's Brewery, Elizabeth Street, Sydney.

December 8th.—The Botanic Gardens, Sydney.

December 9th.—The Shale Oil Development Committee Ltd., Newnes.

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

PHYSICAL SCIENCE.

Officers: *Chairman,* Professor O. U. Vonwiller B.Sc., F.Inst.P.; *Secretary,* Assistant Professor G. H. Briggs, B.Sc., Ph.D., F.Inst.P.; *Assistant Secretary*, S. E. Williams, B.Sc.; *Committee,* Professors Bailey, Madsen, Wellish, Major E. H. Booth, Mr. J. Bannon, Miss P. Nicol.

The Section, during the year 1931, made certain changes in the conduct of its affairs, which are briefly as follows:—The Committee decided to formally associate in future, with the Section, advanced students of Physics in the University of Sydney and others not eligible for membership of the Royal Society; such members of the Section to elect two representatives to the Committee of the Section, one of whom may act as Assistant Secretary of the Section.

Thirteen meetings were held during 1931, the average attendance being 14.

April 15th, 1931.—Mr. Bannon—Demonstration and description of the Methods used in the Radium Laboratory, University of Sydney, in the purification of Radon.

April 29th, 1931.—Joint discussion with the N.S.W. Branch of the Royal Astronomical Association on the Constitution of Stars.

May 13th, 1931.—Mr. J. Raynor, B.Sc.—Electrical Methods of Geophysical Prospecting.

June 10th, 1931.—Associate Professor Bailey—Some Recent Scientific Experiences and Impressions in Europe.

June 17th, 1931.—Mr. R. L. Aston, M.Sc.—Milne's Theory of Stellar Constitution.

July 1st, 1931.—Mr. S. E. Williams—Atmospheric Potential Gradient: Its Measurement and Correlation with Meteorological Conditions.

July 15th, 1931.—Mr. G. Godfrey—The Mathematical Basis of Einstein's Unified Field Theory.

August 5th, 1931.—Professor V. A. Bailey—Some New Phenomena associated with Beams of Electrons.

September 16th, 1931.—Discussion of Professor Wellish's paper on Photoelectrons and Ions.

October 7th, 1931.—Discussion of Photographic Methods of Measuring Radiation Intensities.

October 22nd, 1931.—Assistant Professor G. H. Briggs—Recent work on the Relation of alpha and beta rays to gamma rays. Mr. H. J. Frost—Some curves obtained with thin plates in the infra red.

November 4th, 1931.—Mr. R. L. Aston—Surveying Instruments, with special reference to recent improvements.

November 18th, 1931.—Professor O. U. Vonwiller—Total Reflection of X rays.

THE PRODUCTION OF ZINC BY ELECTROLYSIS OF ZINC SULPHATE SOLUTIONS.*

By Harry Hey.

With five text figures and one plate.

Published as a Supplement to the Journal of the Royal Society of New South Wales, Vol. LXV., 1931.

The public opening of the Faraday Exhibition in London less than 24 hours ago reminds us that it is but 100 years since Michael Faraday made the discovery in which lies the origin of the dynamo, and thus laid the foundation for the development of electrical machinery, which is the basic requirement for any electro-chemical industry. The first commercial "dynamo electric machine" was produced by Siemens in 1867 and from then onwards chemists, physicists, engineers and others have given a great deal of attention to applied electro-chemistry, of which the electrolytic zinc industry is an important branch.

The world's production of zinc during 1930 by all processes totalled approximately 1,400,000 tons, and the present annual capacity of plants using the electrolytic process aggregates approximately 550,000 tons. Australia's share is 55,000 tons, increasing to 70,000 tons when the Risdon extensions are completed. The power required for depositing zinc in the world's electrolytic zinc plants when on full production amounts to a continuous load of 270,000 H.P., D.C.

* First Liversidge Research lecture delivered on 24th Sept., 1931, at Science House, Sydney, arranged by the Royal Society of New South Wales under the terms of the Liversidge bequest.

As recently as 1914 there was no electrolytic zinc industry. Its development has been truly remarkable. Its position to-day is an outstanding example of the application of rigid chemical control to large scale operations. The electrolytic zinc plant is really a laboratory on a large scale in which thousands of gallons, instead of litres, of solution are handled in tanks and pumps instead of beakers and pipettes. The removal of some impurities is carried to a degree farther than was previously necessary for the analytical determination of these same substances; new standards of analysis were necessary and new methods have been devised.

History.

Australia—especially the State of New South Wales—was particularly concerned with the early attempts to develop the electrolytic zinc process. A large quantity of zinc-bearing by-product had accumulated at Broken Hill, and it was thought to be suitable for treatment by some such process.

Prior to 1913 literally hundreds of experimenters attempted to recover zinc by hydrometallurgical processes which, in many cases, involved the electrolysis of a solution of either zinc sulphate or zinc chloride. Accounts of their experiments are distributed throughout the literature of many countries, more especially in patent records, but it was not until 1914 that the modern electrolytic zinc process or, indeed, any commercial process involving the electrolysis of zinc sulphate solutions, can be said to have been established. Small plants were operating earlier in Germany and in England, using a zinc chloride electrolyte, but these plants have been closed and the chloride process abandoned. Unless otherwise specified any further reference will be confined to the sulphate process.

It is instructive to review the outstanding early attempts to produce electrolytic zinc. In 1881 Letrange obtained patents[a] for producing zinc by electrolysing zinc sulphate solutions. His process included roasting, leaching and electrolysis. He used sheet zinc cathodes and carbon anodes, but he did not succeed in producing zinc on a commercial scale. His work is of interest, chiefly because be used insoluble anodes; cells without diaphragms and an electrolyte containing free acid. It has been claimed by Ralston[b] that Letrange practically anticipated modern practice, but as far as can be determined at this date the only feature in common with present practice is the use of sulphate solutions containing free acid.

About 1891 Sherard Cowper Cowles (the inventor of the Sherardising process) was experimenting with the electro-galvanising of iron and steel articles, using zinc sulphate solutions, and some three or four years later he erected an experimental plant in Cornwall for recovering electrolytic zinc from the Broken Hill material already mentioned.[c] He removed copper and cadmium from the impure zinc sulphate solution (obtained by roasting and leaching) with scrap zinc or zinc dust, and he sometimes found it necessary to remove manganese. The solution purified in this way contained approximately 100 grams of zinc as sulphate per litre. He electrolysed with lead anodes and aluminium cathodes and he apparently also recognised that free sulphuric acid in the electrolyte improved the character of the deposited zinc. As far as the author knows, Cowper Cowles was the first experimenter to use aluminium cathodes, and it is likely that he also recognised the need for careful purification of the solution. He did not succeed in establishing the process on a commercial basis.

Probably the most ambitious unsuccessful attempt to produce electrolytic zinc commercially was made by Ashcroft at Cockle Creek, near Newcastle, in New South Wales, in 1897, following upon experiments carried out by him in Broken Hill and in England.[d] It is said that £250,000 was spent on this venture. His original intention was to electrolise zinc chloride solutions, and, in fact, his plant was designed for and operated with such solution for most of its life, but for some weeks the electrolyte was zinc sulphate. He used diaphragm cells fitted with iron or zinc cathodes and lead and carbon anodes.

Ashcroft recognised that copper, iron, arsenic, antimony, etc., were harmful, and he also states that he had considerable trouble with manganese. However, subsequent work with Broken Hill ores has shown that Ashcroft's troubles were due mainly to cobalt, which he unknowingly precipitated when removing manganese from solution.

Early in the twentieth century, Englehart, Huth and Laszczynski, of the Siemens Halske organisation, made notable advances in the subject, particularly in respect of purification of solutions. They recognised that it was necessary to convert iron to the ferric state before it could be satisfactorily precipitated, and, in fact, patented a process involving the use of manganese dioxide for this purpose. Lime or zinc oxide was then added for precipitating the iron and with it certain other impurities, particularly arsenic and antimony, together with silicic acid. The staff of this organisation also proposed the use of moulded manganese dioxide anodes, but this type of anode has not been adopted in any commercial plant.

About 1910 the General Electric Company of America developed a sulphate process, the original basic feature of

which was the maintenance of a neutral electrolyte by feeding zinc oxide directly to the cells. Under these conditions the zinc deposit was spongy. Some years later an electrolyte containing free acid was investigated and Hansen, of this organisation, collected much instructive data respecting roasting, leaching, purification and electrolysis.[e]

All this preliminary work—some of it expensive—had failed to establish the process on a commercial scale, but it had served a very definite and useful purpose by indicating some of the pitfalls and had shown that the removal of certain impurities from the solution was essential for successful electrolysis. It is perhaps unfortunate that there was a mistaken idea that the electrolytic zinc process could only be justified for the treatment of those complex ores which could not be economically treated by the older distillation process. These ores contained many interfering substances (some of which consumed acid), and others were very definitely toxic, in that their presence in the electrolyte, in many cases even in minute quantities, prevented the satisfactory deposition of zinc. Most of the ores also contained excessive silicious material which formed soluble silicates during roasting.

The successful commercial production of eletrolytic zinc was established with the completion of the plants erected in 1915 at Great Falls, Montana, U.S.A., by the Anaconda Copper Company, and simultaneously at Trail, British Columbia, Canada, by the Consolidated Mining & Smelting Company. These plants were erected primarily to satisfy the urgent demand for pure zinc for use in the manufacture of high grade brass, etc., required for munitions. Their construction followed an extensive series of investi-

gations, not only connected with the process reactions, but concerning the equally important development of the most suitable equipment, and it is to the credit of the organisations responsible that the modern equipment, and, in essentials, the process, is but little changed from the plants erected in 1915 and the practice followed there. The Tainton process, referred to later, is an exception to this generalisation.

Interest in the process was rekindled in Australia in 1916, when attempts were made to treat Broken Hill concentrates at Bully Hill, California, and at Broken Hill. Preliminary work showed that electrolytic zinc could be satisfactorily produced, but only after the recognition that cobalt was present in the Broken Hill concentrates and that it was a toxic impurity. In 1917, the first small scale plant was erected at Risdon, producing a few pounds of zinc per day; this was followed by a somewhat bigger plant, and this again by another which had an ultimate output of 25 tons per day. The latter plant was used for providing data on which to design the present plant which has an output of approximately 150 tons slab zinc per day.

Since 1917, many refinements have been introduced at all the plants, but the main principles of the process remain unaltered. There have certainly been many changes in practice which have enabled the recovery of zinc to be increased and/or costs to be reduced. This is the natural result of continued extensive research, both pure and applied, and to-day electrolytic zinc containing more than 99.9% zinc can be produced as cheaply as, if not more cheaply than, retort spelter of considerably lower grade produced by the old-established method of distillation from a mixture of zinc oxide bearing material and carbon.

Outline of Present Practice.

The three major objectives of the electrolytic zinc metallurgist are:—

(a) Recovery of the maximum amount of zinc as zinc sulphate in solution from a given raw material;

(b) Removal of dissolved impurities to the required degree as cheaply as possible and with the minimum loss of zinc; and

(c) The deposition of zinc of maximum purity and satisfactory physical condition from the purified solution with the minimum power consumption.

These objectives are all inter-related, and to attain them the various operations, comprising the electrolytic zinc process in toto, have necessarily to be carried out under carefully controlled conditions.

The process is a cyclic one and the sequence of steps is:—

(1) Roasting the raw zinc sulphide material under such conditions that the zinc sulphide is converted to zinc oxide and a controlled amount of zinc sulphate.

(2) Leaching or dissolving the zinc oxide from the calcines produced in step (1), using spent electrolyte produced in step (4).

(3) Purification, or removal of those impurities which either interfere with the electrodeposition of zinc or contaminate the deposit.

(4) Electrolysis of the purified solution whereby it is depleted of portion of its zinc with the regeneration of equivalent sulphuric acid for re-use in the leaching step.

(5) Melting the cathode zinc produced in step (4) and casting the molten metal into ingots for sale, and

(6) Treatment of these residues or precipitates which contain substances having some value.

Nature of Zinc Bearing Material Treated.

Most of the raw material is obtained from mixed lead-zinc ores, which are treated by the flotation process for the production of lead and zinc concentrates. The former contains the bulk of the lead sulphide and the latter consists mainly of zinc sulphide contaminated with iron and other sulphides. The iron may be present as pyrrhotite or pyrite. Sometimes the former is free; sometimes it is in solid solution in the zinc sulphide mineral.

In addition, practically every zinc concentrate contains some siliceous gangue and traces of other impurities which, whilst small in amount, have a significant effect on the subsequent treatment of the concentrates and/or products obtained therefrom.

The zinc concentrates supplied to electrolytic zinc extraction plants contain 45-60% zinc, 4-12% iron and some lead and silver—all as sulphides.

Impure zinc oxide produced from lead blast furnace slag is also used at two plants.

Roasting.

The primary object of roasting is to convert the various sulphides to oxides. When a mixture of the sulphides of zinc and iron is heated under oxidising conditions such as apply during commercial roasting, some of the iron oxide combines with zinc oxide to produce zinc ferrite ($ZnO.Fe_2O_3$). As this substance is relatively insoluble in dilute sulphuric acid, any zinc oxide so fixed is not recovered during leaching. The amount of ferrite formed depends on the grain size of the iron oxide and zinc oxide and also upon the temperature at which the two oxides are in contact.

When the zinc mineral contains iron sulphide in solid solution the two oxides are formed in molecular contact, and under these conditions the whole of the iron oxide will combine with equivalent zinc oxide irrespective of roasting temperature. On the other hand, where the zinc sulphide and iron sulphide are in separate minerals, combination between the oxides can be minimised by controlling roasting temperature; for example, if a mixture of zinc oxide and ferric oxide in the ratio of 2 ZnO to 1 Fe_2O_3 be heated at 700°C for 4 hours, 36% of the iron oxide is converted to ferrite. At 1000°C the conversion is 87% in the same period.[g]

Practically all the iron sulphide in the Broken Hill zinc concentrates is in solid solution in the zinc mineral, and consequently temperature control during roasting is not important, excepting in-so-far as it affects the output of any given furnace. The other notable Australian zinc-bearing ore—the Rosebery-Hercules ore of Western Tasmania—contains a small amount of iron in the zinc mineral and, in addition, much free pyrite, some of which is recovered in and contaminates the zinc concentrate. In this case roasting temperatures therefore affect the amount of zinc ferrite formed.

The silica contained in zinc concentrates is important because some of it always combines with the oxides of zinc and lead during roasting, and the amount increases with increasing temperature. The resulting silicates are soluble during leaching.

The figures of Table 1 represent the effect of roasting temperature on the solubility of the various impurities in dilute sulphuric acid. The amount of each impurity is relative to 100 grams of zinc.

TABLE I.

Relationship between Roasting Temperatures and Solubility of various impurities in Calcines produced from Broken Hill concentrates containing 49% Zinc.

Roasting Temperature.			700°C.	800°C.	900°C.
Zinc	dissolved,	Grams ..	100	100	100
Mn	,,	,, ..	0.90	1.10	1.58
Total Fe	,,	,, ..	0.70	0.55	0.71
Fe (ous)	,,	,, ..	None	None	None
SiO_2	,,	,, ..	1.29	2.97	3.85
Cu	,,	,, ..	0.38	0.25	0.26
Cd	,,	,, ..	0.45	0.40	0.25
Ag	,,	mgs. ..	30	56	75
Sb	,,	,, ..	3.2	1.4	0.9
Co	,,	,, ..	12.9	12.9	13.3
Cl	,,	,, ..	Trace	Trace	Trace

With increasing temperature the amounts of soluble manganese and silver increase, but less copper, cadmium and antimony dissolve.

As the result of improvement in metallurgical practice in Broken Hill, the zinc concentrates now produced there contain 52½% zinc, less silica and less copper than formerly.

Roasting is usually carried out in multiple hearth furnaces, and at most plants it is done in one operation. In Australia roasting is done in two stages. The first stage is carried out on the mainland at locations adjacent to superphosphate plants. The sulphur is reduced from 30% to 6%, of which 1½ to 2% is sulphur remaining as sulphates of lead, calcium and zinc. Sulphuric acid is produced from the sulphur dioxide contained in the roaster gases. Both the chamber and contact methods of making sulphuric acid are used.

The normal annual output of the Australian acid plants utilising zinc concentrate gases is equivalent to 70,000 tons of 100% acid when on full production. From this 215,000 tons of superphosphate are manufactured.

Considerable research was necessary before the manufacture of contact acid from zinc concentrate roaster gas became an established process, because the roaster gases contain interfering amounts of arsenic and chlorine compounds in addition to lead sulphate and calcine dust. Some of these impurities settle in dust chambers, but final purification is effected by saturating the gases with water and passing them through an electrostatic precipitator. The removal of lead sulphate, arsenic and chlorine compounds during this treatment is 100%, 99% and 92% of the respective amounts of these impurities entering the electrostatic precipitator.

The gases are subsequently washed to remove the remaining chlorine compounds, are dried and are passed through a platinum contact mass. This mass has now been in use for over four years without regeneration.

The roasted concentrates or pre-roast calcines produced at the various mainland roasting plants are forwarded to Risdon, and are subjected to the second or re-roasting stage, in which sulphide sulphur is reduced from 4½ to 0.5%, and the sulphate sulphur increased to whatever is necessary to replenish any mechanical or chemical losses of sulphuric acid or zinc sulphate during leaching. This at Risdon is equivalent to 3% sulphate sulphur in the calcines leached.

Another important function of the re-roasting operation is the elimination of chlorides which contaminate the partly roasted calcines. These are introduced at the various roasting plants in the water used for wetting these calcines to minimise dusting during shipment to Risdon.

Chrome steel has replaced the cast iron and cast steel previously used for roasting furnace rabble arms. The Australian furnaces used in the first stage have been fitted

since 1920 with rabbles of alloy steel containing 27% chromium. This steel will withstand a temperature of 900°C continuously for 12 months or more without serious oxidation or failure from other causes. Other alloys containing chromium, nickel and tungsten or silicon are giving encouraging results at Risdon.

Leaching.

The spent electrolyte returned to the leaching plant from the electrolytic cells is of varying sulphuric acid concentration. The concentration is fairly regular from day to day at any one plant. Only portion of the zinc is removed during electrolysis; therefore all these solutions contain zinc sulphate.

Three distinct methods of leaching are practised at various plants. These are:—

(1) Batch leaching, where the roasted zinc concentrate, usually referred to as calcines, is added to a given volume of leach solution. It is usual to add the calcines in more than one stage and to continue this addition until the acidity of the solution has been reduced to a predetermined figure. The solution obtained is subsequently treated for the removal of iron, arsenic, antimony and silver, which is referred to later.

(2) Two-stage continuous counter-current leaching, the equipment for which consists of two series of leaching vessels, four or more in each series, together with settling or thickening equipment. Partially leached calcines and spent electrolyte are fed continuously into the first vessel of one or "acid" series. During its passage through the series the zinc oxide is completely dissolved. The mixture overflows the

last vessel of the series and is settled and filtered. The residues are discarded. The solution which still contains acid is mixed with new calcines and fed through the second or "neutral" series of leaching vessels in which the acid is completely neutralised, but only portion of the zinc oxide is dissolved from the new calcines. There thus remains free zinc oxide, some of which reacts with and precipitates the iron, arsenic, antimony, silica and some of the copper which had dissolved during the other leaching stage. The mixture is settled and the solution overflowing the settlers or thickeners is sent forward to the purification section. The settled solids are mixed with spent electrolyte and the mixture is sent on to the first leaching stage.

At some plants the spent electrolyte is divided over both stages, but in all cases the solution overflowing the "acid" leaching series contains free acid and the overflow from the "neutral" series is neutral or basic.

(3) For this method of leaching the calcine is separated into two products—a magnetic portion, which contains the bulk of the zinc ferrite, and the non-magnetic portion, which is said to contain the free zinc oxide and any gangue material. As ferrite is soluble in sulphuric acid of moderate strength at relatively high temperatures, the magnetic portion is first leached with the spent electrolyte, and after most of the ferrite is dissolved, the non-magnetic portion is added to the partially neutralised solution which, incidentally, contains ferric sulphate equivalent to the zinc ferrite dissolved. The iron is precipitated as basic sulphate along with silica, and

these remain with the insoluble portion of the residues after settlement and filtration.

This method, (3), which can be operated either continuously or intermittently, is usually only applied where high acid spent electrolyte is available. Filtration which is difficult enough with a saturated solution of zinc sulphate is made more difficult by the presence of much basic sulphate of iron. The method was developed in conjunction with the Tainton process which operates under high acid electrolysis conditions.

The batch method (1) was the procedure originally followed at the Trail and Anaconda plants, and, after leaching, a small amount of lime or limestone was added to the mixture of residue and solution to precipitate iron, silica, arsenic and antimony. Since 1920, however, the second method has been applied at these plants and it has become the general practice at most of the more recent plants.

The advantages of the second method are:—

(a) The solution, immediately prior to leaving the leaching circuit, is in contact with zinc oxide, thus ensuring nearly complete precipitation of iron, arsenic and antimony, and

(b) The residues are discarded from an acid pulp; the maximum amount of zinc oxide is thus recovered.

Its disadvantages are:—

(c) The residues are thickened twice, and

(d) The discarded residue contains the precipitated silicic acid and basic iron salts which make filtration difficult.

A modification of the batch leaching as described under (1) is used at Risdon and leaching is continued until the acidity is reduced to two grams sulphuric acid per litre. When separated from the solution, the residues, which are practically free from precipitated iron or silica, are in a satisfactory physical condition for subsequent treatment for recovery of lead and silver.

The residues from the leaching stage contain zinc ferrite and zinc sulphide which was not oxidised during the roasting of the zinc concentrates, and some undissolved zinc oxide, together with insoluble gangue material. The zinc sulphide and zinc oxide are contained in the coarser particles, and at Risdon this coarse material is separated from the finer residues and is subjected to further treatment which comprises, firstly, fine grinding and leaching with spent electrolyte, and, secondly, treatment in flotation machines for the recovery of the zinc sulphide as a concentrate which is roasted and leached. The residues from the flotation machine join the fine residues from the major leaching operation and the mixture is settled in thickeners. The settled solids are then filtered.

The filtered residue contains most of the lead and silver originally in the concentrates and is shipped to Port Pirie for treatment.

Purification of the Solution.

Removal of Iron, Silica, Arsenic and Antimony.. The zinc sulphate solution obtained by applying the two-stage continuous counter-current leaching method (2) is practically free from iron, arsenic and antimony, and the silica which dissolved has been precipitated. These impurities have been discarded in the leach residues. The solution still contains copper, cadmium and manganese, and in some cases cobalt. On the other hand, the solution obtained at

Risdon by the single stage batch process contains all the impurities dissolved during leaching in addition to 2 grams free sulphuric acid per litre. Neutralisation of the acid and precipitation of the iron, silica, antimony and arsenic is effected by treatment with finely ground limestone and the precipitate—which is composed mainly of gypsum, basic ferric sulphate and hydrated silica—is coagulated by prolonged agitation. For rapid filtration it is essential that there be sufficient gypsum crystals in the precipitate to provide a support for the gelatinous iron and silica precipitates. The presence of ferric iron is necessary for the removal of arsenic and antimony.

The modus operandi at Risdon is the result of considerable investigation and, so far as the author knows, it is the only plant where this procedure is followed. The precipitate contains a small amount of coagulated silver chloride, which is removed by washing the filtered precipitate with sodium thiosulphate. The wash water goes forward with the main solution.

With any method of leaching it is necessary to convert any dissolved ferrous sulphate to the ferric condition. Agitation with air during leaching usually does this but it is necessary to add manganese dioxide when much ferrous iron is present.

The recovery of zinc from the calcines is determined largely by the thoroughness with which the residues and, at Risdon, the limestone precipitate, are washed. Because of the cyclic nature of the process, the permissible amount of wash water is definitely limited to the amount of the solution discarded with the residues and the water lost by evaporation, due to circulation of the solution. Water was originally added to the calcines at Risdon to minimise

dusting during the handling of this material between the reroasting furnaces and the leaching section. In recent years, however, zinc sulphate circuit solution has been substituted, and thus no new water goes into the circuit at any point other than as wash water through the residues or limestone and other precipitates.

The circuit solution is cooled at Risdon by running it down towers under conditions whereby cooling of the solution is brought about by evaporation of water. Water equivalent to that evaporated is available for use as wash water.

Removal of Copper and Cadmium. The next stage in the preparation of the solution is the removal of copper and cadmium. Hydrogen sulphide and various sulphides have from time to time been proposed for this purpose, but zinc dust is in universal use. Nearly complete removal of copper can be effected by agitating the solution with equivalent zinc dust, but the precipitation of cadmium requires excess over that theoretically necessary. Most of the antimony and arsenic which has escaped precipitation during the preceding step is removed with the copper and cadmium.

In the original Anaconda plant, the mixture of zinc dust and solution was agitated by using compressed air, and this practice was followed until recent years. The trend at Risdon has been to take extreme precautions against introducing air into the purification tanks; in fact, the purification section was remodelled some time ago in order to prevent ingress of air through the glands of the pumps handling the mixture of precipitated copper and cadmium and solution between the tanks and the filter presses.

The solutions at Risdon prior to zinc dust purification contain approximately 250 mgs. of cadmium and 200 mgs.

of copper per litre, but the amounts vary over a fairly wide range from day to day. In order therefore to confine the consumption of zinc dust within the lowest possible limit, it is an advantage to know the actual concentration of copper and cadmium in the solution going to the purification tanks. Within the last year a method has been developed at Risdon for the quick electrolytic estimation of copper and cadmium, using a mercury cathode. Analyses obtained in this way are used as the basis for calculating the amount of zinc dust to be added.

At the present time the precipitation of the two impurities is done in batches. An ingenious continuous process has been developed, but for economic reasons it has not been adopted.

At most of the electrolytic zinc plants, the solution is suitable for electrolysis after treatment with zinc dust. It is true that many of the zinc concentrates treated in these plants contain some cobalt, but usually in insufficient amounts to cause trouble during electrolysis. It accumulates in the circuit solutions until the concentration is such that the amount of solution discarded from the plant in the various residues contains as much cobalt as is introduced each cycle. For example, if one-tenth of a milligram of cobalt per litre were introduced during each leaching cycle, and if 1% of the circuit solution were discarded as indicated, the amount of cobalt discarded would be equivalent to the amount introduced when the concentration in the circuit solution reached approximately 10 mgs. per litre.

Removal of Cobalt.—At Risdon appreciable amounts of cobalt dissolve from the Broken Hill concentrates, and the amount dissolved in each cycle must be removed. Because of this the Risdon practice from this stage

onwards differs from most of the other plants. Zinc dust will precipitate cobalt from a water solution of its sulphate, but has very little effect in the presence of a large amount of zinc sulphate; consequently, the removal of cobalt during zinc dust treatment is negligible.

Many reagents oxidise cobalt if manganese is also present, and in this condition it is easily precipitated. The permanganates, lead peroxide and calcium plumbate, have been used for this purpose. With solutions containing much manganese, as is the case at Risdon, the cost of these reagents is excessive because it is necessary to oxidise all the manganese before the cobalt can be precipitated. Methods based on the use of the reagents mentioned have been investigated at Risdon, but only two methods which are of a different type have been used on a plant scale. These are:—

(1) The so-called "arsenic purification" method, in which cobalt is co-precipitated with arsenic and copper by the addition of zinc dust. In practice, sodium arsenite and copper sulphate are added to the solution, which is heated and then treated with zinc dust. The cobalt, arsenic and copper are precipitated together. It is an expensive method, because zinc dust consumption is high and it is necessary to heat the solution.

(2) The precipitation of cobalt by nitroso beta naphthol from the cold copper and cadmium-free solution. This was suggested in 1917, but has only been applied regularly on a commercial basis during recent years. In practice the calculated amount of sodium beta naphtholate is added to the solution, then sufficient sodium nitrite and finally sulphuric acid to form the nitroso salt in

the solution. The cobalt is precipitated as the characteristic red cobalt-nitroso beta naphtholate, and the mixture of the precipitate and solution is neutralised with sodium carbonate. About $9\frac{1}{2}$ lbs. of beta naphthol and equivalent sodium nitrite are required for precipitating 1 lb. of cobalt.

The latter method has entirely superseded the "arsenic purification" process, and is one of the major developments which has rendered possible the change in electrolytic procedure which is referred to later.

The cobalt in the solution feeding the electrolytic cells at Risdon is maintained at about 10 mgs./litre. The spent electrolyte contains a similar amount. Approximately 10 mgs. are introduced into the solution, each leaching cycle, and thus the solution after leaching contains 20 mgs./litre. It is therefore necessary to remove cobalt from 50% of the solution, each cycle to maintain the required concentration in the feed to the cells. About 60lbs. of cobalt are removed from the solution daily. Until two years ago the Risdon electrolyte contained 70-80 mgs. cobalt per litre, and the removal of cobalt from a much smaller volume of the solution was sufficient to maintain the cobalt concentration constant.

Removal of Chlorides.—The other purification stage concerns the removal of chlorides. The electrolyte is maintained at about 75 mgs. chlorine as chlorides per litre, and it is necessary to purify sufficient solution to take care of any chlorides introduced during leaching. The precipitation is effected by silver sulphate; the silver chloride produced is separated by filtration and is reconverted to silver sulphate by treatment with zinc dust and heating with sulphuric acid, when hydrochloric acid is volatilised to waste.

Those portions of the solution treated for removal of cobalt and/or chlorine join the main copper and cadmium-free solution. The combined solution after addition of glue is in suitable condition for electrolysis.

At Risdon the daily volumes of solution treated in leaching and the various purification stages are:—

During leaching	600,000 galls. — 16,000 gallon batches.
For removal of Iron, Arsenic, etc.	600,000 galls. — continuously.
For removal of Copper and Cadmium	600,000 galls. — 14,000 gallon batches.
For removal of Cobalt	300,000 galls. — 14,000 gallon batches.

Portion of the solution is treated intermittently as required for removal of chlorine.

In some stages the circuit solution is very corrosive, as it contains ferric and copper sulphate and free acid. There have been many corrosion problems in connection with pumps, filters, launders and tanks. It has been found that celery top pine grown in Tasmania resists the action of acid zinc sulphate solution better than does any other timber yet experimented with at Risdon. Acid-resisting bronze and Staybrite are used for some metal parts, but wherever possible the flow sheet of the plant is arranged so that corrosive solution flows by gravity through lead pipes.

Over 100 tons of leach residues and 30 tons of limestone precipitate are filtered from the solution each day. Filtration problems arise and they are investigated, with the result that the filtration technique has gradually improved over a period of years.

The partial analysis of the solution after purification is given in Table II.

TABLE II.

Analysis of Risdon Cell Feed Solution.

Zinc	= 114.9 g/l	Total Nitrogen	= 245 mgs/l
Manganese ..	= 13.1 „	Ammonia Nitrogen	= 215 „
Magnesium ..	= 1.75 „	Nitrite „	= 9 „
Sodium	= 9.16 „	Calcium	= 440 „
Potassium ..	= 1.71 „	Phosphate (PO_4)	= 2.1 „
Sulphate (SO_4)	= 222.22 „	Aluminium ..	= 0.5 „
Cobalt	= 10.0 mgs/l	Lead	= 0.025 „
Copper	= 0.6 „	Bismuth	= Nil
Cadmium	= 6.4 „	Nickel	= Nil
Silica	= 80.0 „	Selenium	= Nil
Chlorine	= 75.0 „	Tellurium	= Nil
Iron	= 1.55 „	Tin	= Nil
Arsenic	= < 0.1 „	Glue	= 27 mgs/l
Antimony	= 0.11 „		

The Specific Gravity is 1.334.

The solution is analysed daily for zinc, cobalt, antimony, copper, cadmium and chlorides. Rigid control during purification and accurate analysis enable the concentration of impurities in the cell feed solution to be maintained within very narrow limits.

Electrodeposition.

All zinc sulphate solutions are electrolysed under the general conditions of the two following processes:—

(1) The so-called low acid, low current density process where the feed solution contains 100 to 150 grams of zinc per litre. The sulphuric acid concentration during electrolysis is 90 to 140 grams per litre, and the current density varies between 25 and 45 amperes per square foot at various plants. The zinc and acid concentration and current density are maintained at fairly constant figures at any one plant.

(2) The Tainton high acid, high current density process operating with feed solution containing 215

grms./litre zinc. The acidity of electrolyte is maintained at 280 grms./litre sulphuric acid, and the current density is 100 amperes per square foot.

The end products of electrolysis are zinc, sulphuric acid equivalent to the zinc, manganese dioxide, oxygen and some hydrogen. Portion of the hydrogen is produced by the direct electrolysis of water, but some results from the re-solution of zinc already deposited.

The so-called low acid, low current density process is applied at Anaconda, Trail, Risdon and other plants, and in fact, about 95% of the world's output of electrolytic zinc is produced by this process. Certain advantages have been claimed for the Tainton high acid process, principally in connection with the capital cost of plant because of the smaller volume of solution to be treated for a given output of zinc, and because of the heavier deposit of zinc per unit of cathode area. Another claim is that the high current density counteracts the effect of impurities in the electrolyte. Actually, there is little, if any, saving in capital costs after providing the more elaborate plant necessary to treat a hot, practically saturated, solution of zinc sulphate and to withstand the more corrosive high acid solution. Furthermore, electrolysis is conducted at a very high acidity in order to keep power consumption within reasonable limits, and thus most of the benefit expected from using a high current density is not realised in practice.

In the plants using the low acid, low current density process the cells are rectangular boxes constructed either of timber, lead lined, or of concrete, lined with a mixture of sulphur and sand. They are in series, usually six in number, and are so arranged that the spent electrolyte overflows the first cell of the series into the second and so on through the whole series.

The cathodes at all plants are aluminium sheets, $\frac{1}{8}$in. to $\frac{3}{16}$in. thick, from 2ft. to 3ft. long by 2ft. wide. The sheet aluminium is riveted to a copper head-bar which rests on the busbar. The anodes are cast lead, $\frac{3}{16}$in. or more thick, and are usually somewhat smaller than the cathode in area. Each anode is cast around a copper head-bar, which rests on the appropriate busbar. The anodes quickly become coated with lead peroxide or manganese dioxide or a mixture of the two, and these oxides form the actual anode surface.

The number of cathodes in each cell varies at different plants. They are connected in parallel to the cathode busbar, and the anodes are hung between cathodes and are also connected in parallel to their busbar. The space between the surfaces of the cathode and anode varies from $1\frac{1}{2}$in. to $2\frac{1}{4}$in. at different plants.

The neutral purified solution is usually fed in parallel and in equal amounts to all the cells in one series, or else to all cells excepting the last in the series. Thus the acidity in each of the cells to which feed solution is added is identical.

There are 504 cells at Risdon arranged in three large units of 144 cells each and 1 small unit. Each cell contains 33 cathodes and 34 anodes. The submerged area of both sides of each cathode is 13.0 sq. ft. and the corresponding area of the anode is 11.15 sq. ft. There are approximately 16,000 cathodes in constant use with an aggregate area of more than 200,000 sq. ft.

The electrical circuit in each 144 cell unit is approximately 12,000 amperes at 520 volts, which is equivalent to 3.61 volts per cell.

Each cell is provided with cooling coils, through which cooled water is circulated in amount sufficient to maintain

the temperature of the electrolyte within the prescribed limits.

Diaphragms are not used in any modern zinc cell.

The objective during electrolysis is the maximum economic yield of zinc from the available power. It is possible by costly purification and extra cell-room supervision coupled with the removal of the deposited zinc at more frequent intervals to appreciably increase the yield per unit of power beyond that attained in practice, but the electrolytic zinc industry is like every other industry in that any increase in technical efficiency must always be compared with the cost of obtaining it.

In the literature concerning zinc electrolysis, frequent reference is made to "Current Efficiency," "Cell Voltage" or "E.M.F." and "Yield of Zinc per Unit Power." A definition of each of these terms follows:—

Current or Ampere Efficiency is the yield of cathode zinc expressed as a percentage of that theoretically possible from the current employed in the cell. The theoretical yield is 1.219 grms. of zinc per ampere hour.

The Cell Voltage or E.M.F. is the drop in potential across the cell between the terminals of the anode and the cathode, and is the sum of the anode potential, cathode potential and the volt drop due to the resistance of the electrolyte. The anode potential may be defined as the difference in potential between the anode and the solution immediately in contact with the anode. The cathode potential may be similarly defined as the difference in potential between the cathode and the solution in contact therewith. It is obvious that with a given current efficiency, the energy consumption in the cell is directly proportional to the cell voltage.

The Yield of Zinc per H.P. Day or Kw. Hour, D.C. is a function of the current efficiency and cell voltage.

The current efficiency is used as a measure of the electrolytic efficiency from day to day with an electrolyte of a given composition and system of electrolysis, and ranges between 90% and 93% at various plants. It varies with minor fluctuations in the purity of the solution, and generally it can be stated that it is a measure of the efficiency of the purification stage of the process and also of the care with which electrolysis is conducted.

Cell voltage, on the other hand, which should be nearly constant from day to day in any given plant, varies between different plants.

The inter-relation between current efficiency, cell voltage and yield of zinc at varying acidity is expressed in Figure I, in which is correlated the data obtained from the laboratory electrolysis of a highly purified solution originally containing 139 grams of zinc per litre. The solution used was the purest it has been possible to prepare at Risdon from the purest available materials. It was electrolysed at the temperature and electrode spacing mentioned. It is not directly comparable with the figures obtained on a Works scale, but any plant solution can be examined in much the same way as the pure solution referred to in the curves, if due allowance is made for deposition time. With pure solutions the time effect is not nearly so marked as when impurities are present.

The variables which affect current efficiency or cell voltage or both, and which therefore must be considered in determining the optimum conditions for the electrolysis of any given solution are:—

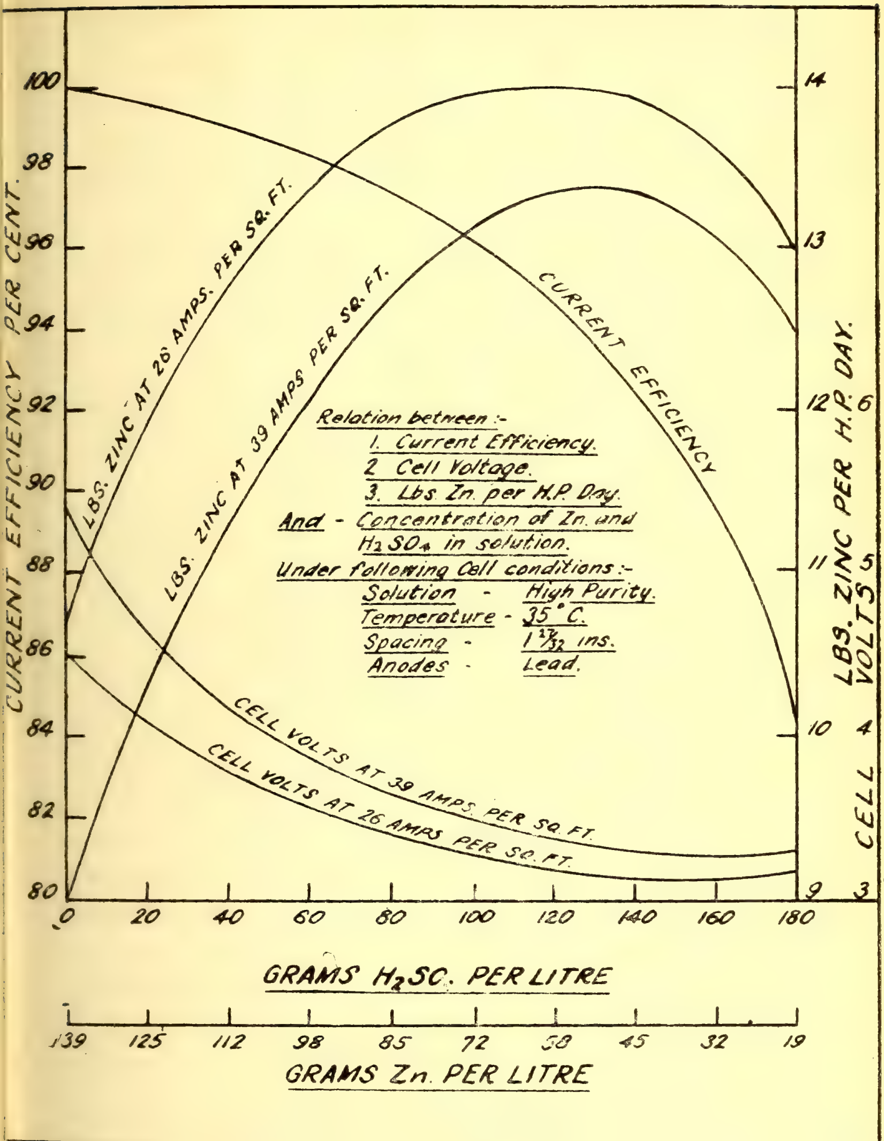

CURRENT EFFICIENCY PER CENT.
100
98
96
94
92
90
88
86
84
82
80
14
13
12
11
10
9
6
5
4
3
LBS. ZINC PER H.P. DAY.
CELL VOLTS
LBS. ZINC AT 26 AMPS. PER SQ. FT.
LBS. ZINC AT 39 AMPS PER SQ. FT.
CURRENT EFFICIENCY
CELL VOLTS AT 39 AMPS PER SQ. FT.
CELL VOLTS AT 26 AMPS PER SQ. FT.
Relation between :-
1. Current Efficiency.
2. Cell Voltage.
3. Lbs. Zn. per H.P. Day.
And - Concentration of Zn. and
H_2SO_4 in solution.
Under following Cell conditions :-
Solution - High Purity.
Temperature - 35° C.
Spacing - $1\frac{1}{32}$ ins.
Anodes - Lead.
0
20
40
60
80
100
120
140
160
180
GRAMS H_2SO_4 PER LITRE
139
125
112
98
85
72
58
45
32
19
GRAMS Zn. PER LITRE

FIG. 1.

(1) *Current Density.* This has little effect on current efficiency unless toxic impurities are present, but the cell voltage increases with increasing current density. It is obvious that whilst a decrease in cell voltage is desirable, a decrease in current efficiency is not.

(2) *Acidity.* An increase in acidity generally reduces cell voltage, but adversely affects current efficiency. The optimum acidity varies according to the amount and nature of the impurities in the solution.

(3) *Zinc Concentration.* This is usually increased when operating with higher acid because C.E. increases with an increase in the $ZnSO_4/H_2SO_4$ ratio.

(4) *Anode Material.* Although lead is used as the original anode, the actual anode surface is usually a mixture of the peroxides of lead and manganese. The presence of certain other oxides derived from impurities in the electrolyte sometimes affects the anode potential and therefore the overall cell voltage.

(5) *Temperature.* Cell voltage and current efficiency both decrease with increasing temperatures with most plant solutions.

(6) *Length of Deposition Period.* Overall current efficiency decreases rapidly with time once cathode corrosion has started.

(7) *Spacing between Electrodes.* The smaller the gap the lower the cell voltage. This benefit is to some extent offset by the greater danger of shorting and consequent reduction in current efficiency.

(8) *Addition Agents.* Substances, such as glue, silicic acid, various gums, etc., are usually added to counteract the effect of impurities.

(9) *Impurities in the Electrolyte,* either dissolved or suspended.

The conditions under which electrolysis is carried out are governed largely by the nature and amount of impurities present in the solution after standard purification; the effect on labour costs, and on the life of the lead and aluminium electrodes.

The more important data respecting the electrolytic practice at Anaconda, Trail and Risdon are:—

	Anaconda	Trail	Risdon Present	Risdon 2 yrs. ago
Zinc concentration of feed solution gm/l	110	150	115	113
Acid in Cell Discharge gm/l H_2SO_4	105	135	90	65
Current Density amp/sq. ft. Cathode	30	30-45	27.5	28
Temperature of electrolyte °C	35-45	30-40	34-37	34-37
Deposition period, hours ..	24	24	72	72

The change from 65 to 90 grams acid at Risdon has appreciably increased power efficiency and was made possible by the substitution of the "beta naphthol" method for the "arsenic method" for removing cobalt. It is now economically possible to operate with an electrolyte containing 10 mgs. instead of 70 mgs. cobalt. Before making the change, 2 years intensive research on electrolysis was necessary and some hundreds of tests were made.

The most notable difference between practice at the three plants mentioned is that of the deposition period, which is three times as long at Risdon as at the other plants. Despite this, the Risdon current efficiency is between 91-92%. For some months, when cathodes were stripped every 48 hours, the current efficiency was approximately 1% higher, and daily stripping gives a still higher figure. The advantages of a 72 hour over 24 hour deposition period

are, firstly, low labour charge per unit weight of zinc produced because the cathodes are stripped less often, and, secondly, the cathode zinc is three times as thick and thus gives a higher yield during melting. The penalties are that the yield of zinc per unit power is somewhat lower, and greater control is necessary in respect of condition of the solution. The balance between the advantages and penalties is dependent largely on the selling price of zinc and on local conditions.

With 24 hour deposition, the Risdon cell acidity could, if desired, be increased to the Anaconda figure and, with increased zinc concentration as well, to that of Trail.

Effect of Impurities on Electrolysis.

All commercial zinc sulphate electrolytes contain impurities, some of which are harmless, some are deposited with the zinc, and others, even when present in small amounts, have a profound effect on electrolysis. The latter are usually referred to as toxic impurities, which include amongst others antimony, cobalt, arsenic, nickel, copper and germanium.

Some impurities which have no deleterious effect when present alone in small amounts sometimes accentuate the toxic effect of others. On the other hand, there is very definite evidence that one, at least, which is generally recognised as toxic has a beneficial effect when used in homeopathic doses under certain conditions. The fact that the joint behaviour of two impurities frequently differs greatly from that expected from their individual effect, undoubtedly explains why there is so much difference of opinion respecting this general question. The effects of the more important impurities have been studied, some in great detail, but in a lecture of this type, generalizations only

can be made, because variations in acidity, etc., have an important bearing on results, and to properly survey the effect of even one impurity would entail a study of a large amount of elaborate data.

Manganese. Of the heavy metals, manganese is by far the most common impurity in the electrolyte; indeed, it is doubtful whether any electrolyte obtained from flotation zinc concentrates is entirely free from it. It accumulates in the circuit until it reaches the concentration at which the rate of deposition as manganese dioxide at the anode balances the amount of manganese sulphate introduced during leaching. The rate of deposition as the dioxide varies with the acidity of the electrolyte, the condition of the anode surface, the nature of other impurities present and the addition agents used. Under present Risdon conditions the equilibrium manganese concentration is approximately 13 grams per litre.

Manganese has little effect on current efficiency under normal conditions, but it does reduce the conductivity of the electrolyte and therefore increases cell voltage. The removal of manganese dioxide which precipitates at the anodes and collects in the lower part of the cell, entails some labour charge. Unfortunately this product always contains lead peroxide and lead sulphate, and thus has little commercial value.

Sodium, Potassium and Manganese Sulphates. These sulphates are all present in the electrolyte and usually have little effect, excepting again on the conductivity of the solution. Some zinc concentrates contain so much magnesium that it is necessary to discard spent electrolyte to maintain a reasonable magnesium concentration in the circuit.

Cadmium. Any Cadmium present in the electrolyte is deposited with the zinc and reduces its grade. Apart from this, it has little effect.

Lead. Lead is present in all cathode zinc and most of it originates from the anode. The condition of the anode surface largely determines the amount deposited with the zinc, and it may be reduced by using a diaphragm between the anode and cathode, which prevents migration of lead. This, however, is not practicable.

Toxic Impurities and Addition Agents. Before discussing the effect of toxic impurities, it is necessary to comment on the use of addition agents which are used during electrolysis to counteract or control the effect of such impurities. Various substances have been suggested, including a number of gums and silicic acid, but glue is the universal reagent, particularly for electrolytes containing cobalt, and its use gives most remarkable results. Most operators use some glue, but because of the relatively large amount of cobalt in Broken Hill concentrates the electrolytic procedure at Risdon has been moulded around its use, and it is probably the most important factor contributing to the successful electrolytic treatment of these concentrates.

The mechanism of the action of glue is as yet somewhat of a mystery. Its effects, however, are most striking. Cathode zinc contains nitrogen, whether as glue or one of the decomposition products is not known. It has been suggested that glue migrates to the cathode and forms a film through which zinc ions can pass, but which resists, for example, cobalt ions. The alternative suggestion is that it forms a complex with cobalt and thus interferes with its deposition. Whilst little is known of the way glue functions, we are grateful for its effect.

The most prevalent toxic impurities present in zinc sulphate electrolytes are cobalt and antimony, but there are usually also traces of copper and arsenic and sometimes nickel.

Various investigators have attempted to determine the effect of both cobalt and antimony, but it is difficult to obtain agreement between the results of the different observers, for the reason already stated that traces of some impurities have a profound effect on the behaviour of others.

The toxic effect of most impurities which reduce current efficiency, is accentuated by increase in time of deposition, concentration of the impurity, temperature of electrolyte, acidity of electrolyte and also by decrease in current density.

Cobalt. The toxicity of cobalt was first recognised during the experimental treatment of Broken Hill concentrates in 1916, and about that time it was discovered that its ill effect could be controlled by addition of glue. The early discovery of the effect of glue enabled the Australian industry to be established on a commercial footing, but despite this, the removal of cobalt or its control during electrolysis has continuously occupied the attention of the Risdon technical staff.

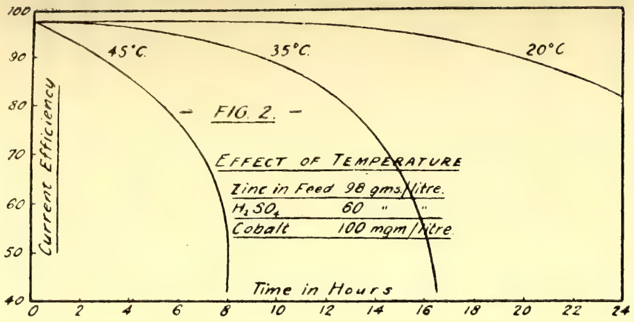
Laboratory studies have been made of zinc sulphate solutions containing cobalt as the only impurity, and of the Risdon plant solutions. Figures 2 to 5 show the effect of temperature, acidity and current density when electrolysing solution (otherwise highly purified) to which various amounts of cobalt have been added. The concentration of zinc, acid and cobalt are stated on each graph. They are not identical in each case, and the ones used were chosen to emphasize the effect of the variable being investigated.

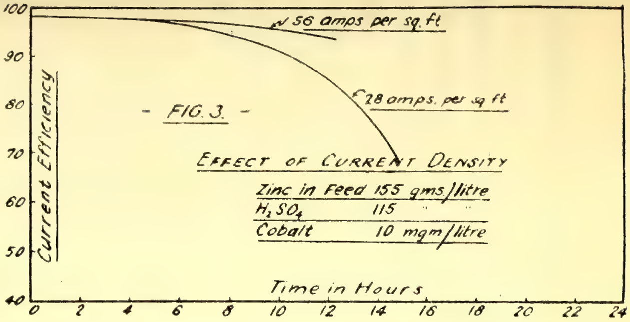
Cobalt was the only impurity in the solution other than traces of silicic acid.

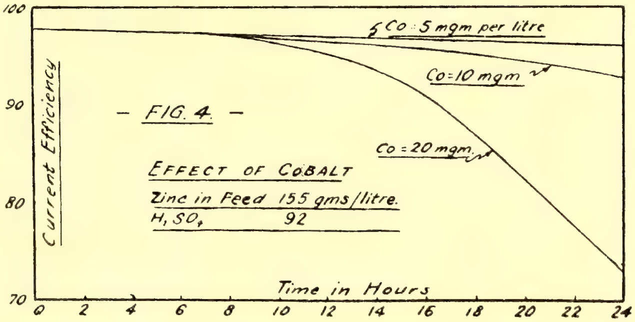
Tests with high cobalt Risdon plant circuit showed that a solution containing as much as 70 mgs. of cobalt per litre, can be electrolysed at 20 grams acid per litre, and 30 amperes/sq. foot to give a current efficiency of 96% during 48 hours deposition without glue. The same solution electrolysed at 55 grams per litre, and with the other conditions unchanged, gave extremely poor cathodes after only 19 hours deposition. No attempt was made to determine current efficiency, as zinc was dissolving from the cathode after 12 hours only, and from then onward current efficiency was nil or thereabout. A similar test was made simultaneously, using glue as an addition agent, and a most excellent deposit was obtained. The solution containing glue could have been electrolysed for 72 hours with good current efficiencies. These two cathodes (a) without glue, and (b) with glue (conditions otherwise similar), obtained after 19 hours deposition are shown in Figure 6. The photograph shows the zinc deposits on the aluminium cathodes.

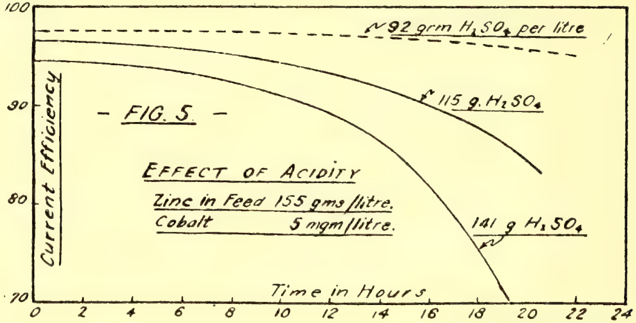
Cobalt has a beneficial effect on the anode potential, and therefore on the cell voltage. With a current density of 30 amps. the anode potential at a lead anode is lowered by 0.15 volts when the electrolyte contains 100 mgs. of cobalt per litre. Assuming an overall cell voltage of 3.65, the reduction is equivalent to 4%, which has a marked beneficial effect on power consumption. Furthermore, the presence of cobalt in an electrolyte restrains the migration of lead from the anode to the cathode, and therefore improves the grade of the zinc deposit.

A considerable amount of data has been accumulated in relation to the effect of cobalt. It is, however, a subject









FACTORS AFFECTING CURRENT EFFICIENCIES OF COBALT BEARING SOLUTIONS

which is intensely interesting and will well repay further study.

For some years the Risdon plant operated on a solution containing 70 mgs. or more of cobalt per litre, and electrolysis was conducted on a 72 hour deposition period with a spent electrolyte containing 65 grams per litre acid, and using 5 to 3 lbs. of glue per ton of cathode zinc deposited. Two years ago the procedure was modified, and the electrolyte now contains only 10 mgs. of cobalt per litre and electrolysis is conducted at 90 grams acid per litre using approximately 1 lb. of glue per ton of zinc deposited. This change, coupled with a reduction in electrode spacing, has enabled the Risdon zinc output to be increased by nearly 10% and, in addition, the structure of the cathode zinc has improved. It is emphasized, however, that the optimum amount of glue addition is dependent on the composition of the electrolyte, and it by no means follows that the conditions found best at Risdon will be applicable to every other solution.

Nickel. Some zinc concentrates contain nickel, which dissolves during the leaching of the calcine. It is toxic even in the absence of cobalt, but more so if cobalt be present. Up to 25 mgs/litre of nickel can be tolerated with little effect on current efficiency, provided cobalt and antimony are low and glue is used. With a solution containing 70 mgs. of cobalt, which, without nickel but with glue yields excellent current efficiencies, 5 mgs. of nickel will cause a drop in efficiency. The amount of nickel in Broken Hill concentrates is insignificant.

Antimony. This impurity shares with cobalt the responsibility for the failure of the early efforts to establish the electrolytic zinc process on a commercial basis, and even since 1914 it has been subjected to considerable verbal

and literary abuse, some of which it undoubtedly deserves. Under certain conditions, however, it has beneficial properties, and for some time antimony was deliberately used at Risdon as an addition agent to maintain the amount of antimony in the electrolyte between 0.2 and 0.3 mgs. per litre.

Zinc deposited from electrolyte containing antimony is rough in structure, and the extent of roughness increases with increasing antimony content. This roughness is particularly in evidence with cobalt-bearing solutions using glue as an addition agent. Figure 7 illustrates the effect of antimony on the structure of cathode zinc. The bulk solution used when producing each of these cathodes was high cobalt Risdon Works solution, from which antimony, arsenic and copper had been removed, and a pure antimony salt then added as required in each case. It contained 80 mgs. cobalt and 100 mgs. glue. The deposition period was 72 hours at 30 amperes/sq. ft., and the temperature was 35°C.

The overall current efficiency when operating with a six-cell series, with 55 grams acid in the first five cells and 65 in the last, would be approximately:—

With less than 0.1 mg. antimony	88% to 90%
With 0.3 mg. antimony	93%
With 0.5 mg. antimony	94%

A variation in the nature and amount of the other impurities would naturally affect the electrolytic behaviour of the solution.

A higher antimony concentration reduces current efficiency, and with the cobalt and glue concentration specified, the optimum amount of antimony is between

0.2 and 0.3 mgs/litre, because with higher amounts the reduction in melting efficiency offsets the gain in current efficiency.

The relationship between cobalt, antimony and glue is obscure, and it is a subject which justifies further investigation.

In a solution free from cobalt or containing a small amount only, antimony has an effect on the structure of the zinc, and it lowers current efficiencies when present in appreciable amounts. The maximum permissible amount varies according to the nature and quantity of other impurities present.

Arsenic. In solutions practically free from cobalt and antimony, arsenic is not very troublesome, but with solutions containing 70-80 mgs. of cobalt per litre and some antimony, less than 1.0 mgs. per litre arsenic has a disastrous effect.

Figure 8a illustrates the cathode zinc produced from a solution free from cobalt and antimony, but containing 5 mgs. arsenic/litre. The current efficiency was over 92% after 72 hours deposition at 100 grams acid/litre.

Figure 8b is a photograph of a zinc deposit produced from solution containing 70 mgs. cobalt and 1 mg. arsenic per litre. The holes are characteristic of arsenic and cobalt together. Despite the presence of glue, the current efficiency was very low after 72 hours at 65 grams acid. The same solution, without arsenic, would have yielded a current efficiency of 88% or better.

In a series of tests using glue and the standard 72-hour deposition period with acidity of 55 and 65 grams per litre, the following efficiencies were obtained:—

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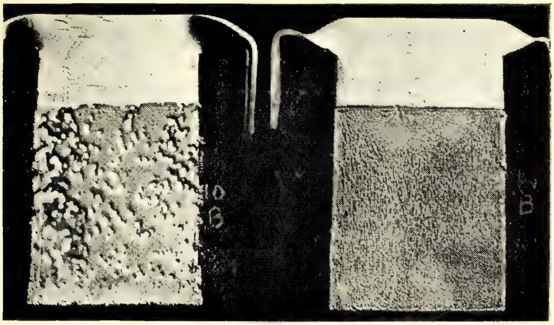
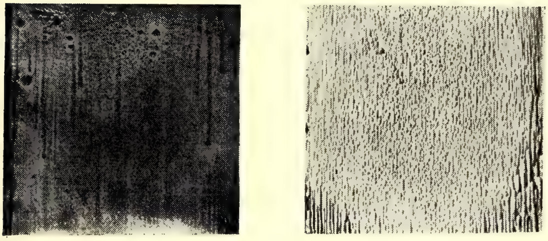
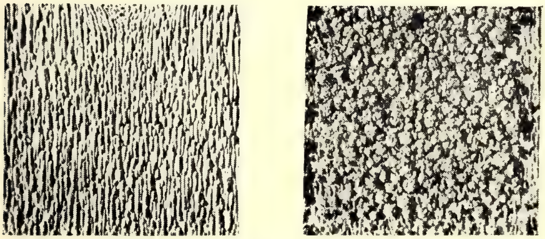


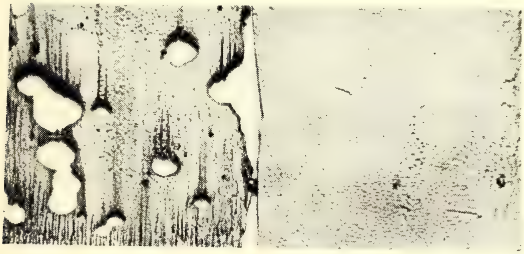
(a) Fig. 6. (b)



(a) (b)



(c) Fig. 7. (d)



(a) Fig 8. (b)

No arsenic	90%
0.25 mgs. per litre arsenic	81%
0.5 ,, ,, ,, ,, ...	73%
1 mg. ,, ,, ,, ...	66%

Copper. Copper is easily removed during treatment of the solution with zinc dust, and a very small amount only is usually present in most commercial electrolytes. With 70-80 mgs. of cobalt, 0.5 mgs. of copper is harmful under some conditions, particularly with increasing acidity of electrolyte and age of deposit. With 10 mgs. cobalt, this amount has little or no effect.

Germanium. Germanium has recently been found in the electrolyte in some of the American plants.(f) This impurity is normally removed during the co-precipitation of the antimony, arsenic and iron. In the absence of sufficient iron, removal of germanium is incomplete, and electrolytic troubles arise. According to Tainton, 0.1. mg. per litre seriously reduces current efficiency. It is possible that antimony has hitherto been blamed for some of the electrolytic effects of germanium.

Other elements have some effect and selenium is notable in that whilst it reduces current efficiency, the zinc produced in its presence is bright and silvery in appearance.

Electrodes.

The condition of the electrodes is important, and one of the major items of expenditure in connection with the electro-deposition of zinc is the cost of replacing anodes and cathodes.

Anodes. Pure lead is used in most plants for anodes, but lead containing 1% silver, and in some cases a little arsenic, is used in the Tainton process. The anode potential

is lower and the cathode zinc contains less lead when lead-silver anodes are used.

Lead containing various amounts of antimony was used in a few cells at Risdon some time ago, primarily as a means of maintaining the optimum amount of antimony in the electrolyte. The zinc produced in the cells using these anodes was rough in structure, and was characteristic of cathodes deposited in the presence of antimony. Despite considerable research by the Risdon staff, using various alloys containing lead as the major constituent, and also with other alloys, no anode material has been developed which is superior to lead.

All lead anodes become distorted during use, and it is a routine duty to keep them straight and spaced correctly. The attention required increases with age, but apart from this there is a relationship between anode age and current efficiency, and it is therefore usual to discard anodes before they are mechanically unsound. This relationship is probably due in some way yet undetermined to intercrystalline penetration by lead peroxide, and possibly other substances. The extent of this penetration is probably partly dependent on the composition of the electrolyte.

Hydrochloric acid in solution corrodes the anodes, and it is mainly on this account that its concentration is maintained at a low figure.

Under the old Risdon conditions the optimum life of anodes is about three years, but the corresponding figure with the Risdon low cobalt solution has yet to be determined. Discarded anodes are re-melted, and the reclaimed lead, amounting to 60 to 70% of that originally in the anode, is utilised for new anodes.

Cathodes. Sheet aluminium is universally used as the base on which to deposit zinc, although attempts have been

made to use zinc sheets. Aluminium-silicon alloy sheets have also been investigated at Risdon. Corrosion of the aluminium above the solution line largely determines the life of the cathode. There is always more or less spray immediately above the electrolyte, and some of this condenses on the unsubmerged portion of the cathode. Furthermore, the solution creeps up the surface, and as the cathode is warm, water is evaporated and acidity increases with consequent acceleration of the corrosion. At some plants the effective life of aluminium is little more than one year, when the cathodes are discarded and sold as scrap.

An investigation extending over several years has been conducted at Risdon to determine the most satisfactory way of counteracting corrosion, and for some time it has been the practice—

(1) To use sheets which are thicker in the unsubmerged portion, and

(2) To further protect this by coating it with a thin deposit of zinc to within an inch or so of the head bar by simply increasing the solution level above normal in a series of cells, in which all the cathodes are electroplated with zinc periodically.

As a result of this strengthening and protection, the cathode life at Risdon was 4 years, until the acidity of the electrolyte was increased two years ago, since when corrosion has been somewhat more marked. There has thus been a further incentive to prosecute the investigation with renewed vigour, and a large number of varnishes, including Bakelite, also rubber and gutta percha, have been applied in a number of different ways without a great deal of success. Covering with lead has been par-

tially successful, but the most satisfactory method is to rivet an aluminium strip reclaimed from discarded cathodes over the unsubmerged portion of the cathodes in use. This procedure is still under test, but it appears likely that it will become standard practice, and the future life of the cathode will probably be determined by the corrosion of the submerged sheet, particularly the edges. This is equivalent to a life of approximately 7 years.

Melting and Casting.

All cathode zinc contains oxygen, and some zinc oxide separates when the cathodes are melted, the amount depending on the structure of the deposited zinc and on the oxidation of zinc during melting.

Two products are recovered—molten zinc and dross—the latter being a mixture of metallic zinc, zinc oxide and coal ash. To facilitate the separation of dross from the molten zinc, it is customary to add a small amount of ammonium chloride. After removal from the melting furnace the dross, whilst still hot, is treated with more ammonium chloride, and most of the metallic zinc is liquidated or ''sweated'' away from the oxide. Finally, after the remaining metal in the dross has solidified, the dross at Risdon is given a light grind, is screened, and the oversize particles, which are mainly metallic zinc, are returned to the melting furnace. This final dross treatment stage yields 1 ton of metallic zinc per day.

The ammonium chloride used at Risdon totals 2lbs./ton of cathode zinc melted.

The melting efficiency, which is the yield of zinc in ingot form expressed as a percentage of the cathodes melted, has now reached 96.6% at Risdon.

Treatment of Residues.

Some of the residues obtained during leaching and purification contain valuable products. Such residues are:—

(1) The leach residues, which retain most of the lead, silver and some of the zinc originally in the roasted zinc concentrates.

(2) The precipitate obtained by treating the solution with zinc dust. This precipitate contains most of the copper and cadmium dissolved during leaching.

(3) The cobalt nitroso beta naphthol precipitate obtained by treatment of that portion of the solution from which cobalt is removed. It is contaminated with zinc sulphate.

Leach Residues.

Various methods have been proposed for recovering zinc from the zinc ferrite in the leach plant residues. Amongst these are:—

(a) Prolonged leaching with hot 10% sulphuric acid.

(b) Treatment with concentrated sulphuric acid and roasting.

(c) Modification of (b) in which roaster gases containing sulphur dioxide are substituted for sulphuric acid, and

(d) Reduction of the ferrite with carbon at a high temperature, and volatilisation of the zinc.

During the leaching with sulphuric acid (Method (a)), the ferrite is decomposed with the formation of zinc sulphate and ferric sulphate, which dissolve. Zinc oxide (as calcines), is added to the solution, and the iron is precipitated as basic sulphate, which is difficult to filter and wash, and contains much adsorbed zinc sulphate.

Method (b) is based on the fact that the decomposition temperature of iron sulphate is lower than that of zinc suphate. In practice acid equivalent to the zinc contained in the ferrite is mixed with the residues, and approximately 40% of the ferrite is decomposed, forming sulphates of iron and zinc. The mixture is heated to a temperature between 650° and 700°C when the iron sulphate decomposes into ferric oxide, and a mixture of sulphur dioxide and trioxide which attacks further ferrite. This cycle is repeated until the whole of the ferrite is converted to zinc sulphate and ferric oxide. The zinc sulphate is dissolved and the solution is added to the main circuit.

In method (c), the hot gases containing sulphur dioxide produced during the roasting of zinc concentrates are passed through the residue maintained at 650-700°C. The end products are much the same as those obtained when roasting with sulphuric acid.

In both methods (b) and (c), zinc is introduced into the circuit as sulphate, and either the sulphate concentration or the volume of the solution increases, unless sulphuric acid in some form or other is discarded from the circuit.

Residues are being leached with sulphuric acid at one plant, and are roasted with acid at another. The fourth method has been proposed from time to time, but as far as the author knows, has not been used commercially for the treatment of leach plant residues. A modification of the process based on roasting the residue with sulphuric acid, has been developed for the treatment of Risdon residues, but whether it is used or not will depend largely on the future price of zinc.

Copper-Cadmium Residues.

The "zinc dust" precipitate contains copper and cadmium, zinc and some silver, and is usually treated for re-

covery of cadmium metal, zinc sulphate solution which is returned to the zinc plant circuit, and a concentrated copper residue containing silver.

The "zinc dust" precipitate produced at Risdon contains:—

Cadmium	11–16%
Copper	8–10%
Zinc	28–32%
Silver	20–50 ozs.

The precipitate is leached in zinc plant electrolyte under conditions whereby most of the zinc and cadmium dissolve together with a small amount of copper. Most of the copper and silver remain in the residue which is filtered, washed, dried and sold.

The resultant solution is agitated with a controlled amount of zinc dust to precipitate cadmium and copper. After separating the solids, the solution is returned to the zinc plant circuit. The precipitate is partly oxidised by drying, and is leached with cadmium plant spent electrolyte. The resulting cadmium sulphate solution is purified and electrolysed. The cadmium cathodes are melted under a flux.

The Risdon production of cadmium is 200 tons per annum.

Cobalt Precipitate.

Cobalt-nitroso beta naphtholate has certain desirable properties as a paint pigment and it is likely that its use for this purpose will become established within the near future.

General.

The industry owes must to research, which in its widest sense relates to electrical, mechanical and chemical engineering, in addition to pure chemistry and physics. In

this connection, it is perhaps not generally appreciated how difficult it sometimes is to interpret the information obtained from laboratory experiments and to use it to improve an industrial process. The first stage in the development of a modification of process frequently involves a large number of experiments in the Work's laboratory, using Work's solution; next comes the development of the technique for maintaining in the plant the optimum conditions determined in the laboratory. An economic study of the laboratory results is then necessary, and in many cases, plant has to be provided, or else the existing plant modified.

The evolution of a process modification from laboratory results is frequently tedious and is a responsible duty. This is particularly true when an alteration of solution composition is under consideration. If done thoroughly, it is undoubtedly an essential part of the research, and without it technical progress would be impossible.

Brief reference has already been made to specific changes in practice developed from research work. The improvement in the Risdon results during the past five years, as shown by various key figures, illustrates the general benefits derived from research work, and from the very rigid control of plant operations to conform with the optimum found during such research work.

The figures for the year ended June, 1926, are compared below with those realised during the year ended June, 1931:—

	Year ended June, 1926.	Year ended June, 1931.
1. Current Efficiency	88.8%	91.6%
2. Yield of Zinc/H.P. Day D.C. in lbs.	10.95	12.23
3. Zinc Dust used for precipitation of Copper and Cadmium in lbs./ton cathode zinc	42	19
4. Melting Efficiency	94.1	96.6%

The author desires to emphasize here, that in the production of electrolytic zinc, and to a greater extent, perhaps, than in the production of any other metal, extraordinarily close control is essential for high efficiency. The process is continuous and operates through every hour of every day in the year. When one realises that small variations in the composition of the electrolyte can produce widely different results, it is evident that the maintenance of high efficiency calls for the closest attention on the part of metallurgists, chemists and operatives generally.

There is still a lot of work to be done before there is a complete understanding of all the reactions which occur during the conversion of zinc sulphide to electrolytic zinc. This is particularly true of the reactions occurring in the cell, and it would be useful to have precise information on the four following matters:—

(1) The reason for the observed effects of toxic impurities;

(2) The manner in which glue and other addition agents restrain the toxicity of cobalt and similar impurities;

(3) The anode reactions, with particular reference to the effect thereon of impurities introduced in the cell feed, and,

(4) The reason why impurities—and antimony in particular—modify the structure of the deposited zinc.

All these matters have had attention at the various electrolytic zinc plants and in university laboratories—in many cases by the various zinc companies' own staffs working there. These reactions are still, however, somewhat imperfectly understood, and there is need for further work.

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Explanation of Plate.

Fig. 6.—Cathode zinc after 19 hours deposition from electrolyte containing 70 mgs. cobalt/litre, (a) without glue, (b) with glue. (See Page M34.) X1/6.

Fig. 7.—Cathode zinc showing effect of antimony in electrolyte (a) Nil Sb, (b) 0.1 mgs. Sb/litre, (c) 0.3 mgs. Sb/litre, (d) 0.5 mgs. Sb/litre. (See Page M37.) X¼.

Fig. 8.—(a) Cathode zinc produced from solution free from cobalt and antimony but containing 5 mgs. arsenic/litre, (b) Cathode zinc produced from solution containing 70 mgs. cobalt and 1 mg. arsenic/litre. (See Page M38.) X¼.

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VOL. LXVI

Parts I and II

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LIST OF THE MEMBERS

OF THE

Royal Society of New South Wales

P Members who have contributed papers which have been published in the Society Journal. The numerals indicate the number of such contributions.

‡ Life Members.

Elected.		
1908		Abbott, George Henry, B.A., M.B., Ch.M., 185 Macquarie-street; p.r. "Cooringa," 252 Liverpool Road, Summer Hill.
1904		Adams, William John, M.I.Mech.E., 175 Clarence-street.
1898		Alexander, Frank Lee, William-street, Granville.
1905	P 3	Anderson, Charles, M.A., D.Sc. *Edin.*, Director of the Australian Museum, College-street. (President, 1924.)
1909	P 9	Andrews, Ernest C., B.A., F.G.S., Hon. Mem. Washington Academy of Sciences: 32 Benelong Crescent, Bellevue Hill. (President, 1921.)
1930		Aston, Ronald Leslie, D.Phil., B.Sc., B.E. *Syd.*, M.Sc. *Cantab.*, Lecturer in Civil Engineering and Surveying in the University of Sydney, 24 Redmyre-road, Strathfield.
1919		Aurousseau, Marcel, B.Sc., No. 65A Market-lane, Manly.
1923		Baccarini, Antonio, Doctor in Chemistry *Florence*, c/o Dante Alighieri Society, Box 1168, G.P.O., Sydney.
1878		Backhouse, His Honour Judge A.P., M.A., "Melita," Elizabeth Bay.
1924	P 1	Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Assoc.-Professor of Physics in the University of Sydney.
1919		Baker, Henry Herbert, Watson House, Bligh-street, Sydney.
1894	P 28	Baker, Richard Thomas, The Crescent, Cheltenham.
1919		Bardsley, John Ralph, "The Pines," Lea-avenue, Five Dock.
1925		Barker-Woden, Lucien, F.R.G.S., Commonwealth Department of Navigation, William-street, Melbourne.
1908	P 1	Barling, John, L.S., "St. Adrians," Raglan-street, Mosman.

Elected.		
1895	P 9	Barraclough, Sir Henry, K.B.E., B.E., M.M.E., M.Inst.C.E., M.I.Mech.E., Memb. Soc. Promotion Eng. Education; Memb. Internat. Assoc. Testing Materials; Dean of the Faculty of Engineering and Professor of Mechanical Engineering in the University of Sydney.
1929		Baur, Fidel George, M.D., Ophthalmic Surgeon, 213 Macquarie-street, Sydney.
1909	P 2	Benson, William Noel, D.Sc. *Syd.*, B.A. *Cantab.*, F.G.S., Professor of Geology in the University of Otago, Dunedin, N.Z.
1926		Bentivoglio, Sydney Ernest, B.Sc.Agr., c/o Tooth and Co., Limited, Sydney; p.r., 14 Gordon-avenue, Coogee.
1919		Bettley-Cooke, Hubert Vernon, F.C.S., A.A.C.I., "The Hollies," Minter-street, Canterbury.
1923		Birks, George Frederick, c/o Potter & Birks, 15 Grosvenor-street.
1916		Birrell, Septimus, Appian Way, Burwood.
1920		Bishop, Eldred George, 8 Belmont-road, Mosman.
1915		Bishop, John, 12 O'Connell-street.
1923	P 4	Blakely, William Faris, "Myola," Florence-street, Hornsby.
1905		Blakemore, George Henry, "Wawoona," 10 Cooper-street, Strathfield.
1888		‡Blaxland, Walter, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, "Inglewood," Florida-road, Palm Beach, Sydney.
1926	P 5	Booker, Frederick William, B.Sc., "Dunkeld," Nicholson-street, Chatswood.
1932		Boon, Herbert Eril, Clerk, University Student and Geologist, 109 Darley-road, Randwick.
1920	P 4	Booth, Edgar Harold, M.C., B.Sc., F.Inst.P., Lecturer and Demonstrator in Physics in the University of Sydney.
1922		Bradfield, John Job Crew, C.B.E., D.Sc. *Eng.*, M.E., M.Inst.E. *Aust.*, Chief Engineer, Metropolitan Railway Construction, Railway Department, Sydney.
1926		Branch, Kenneth James F., 99 Ocean Beach, Manly.
1917		Breakwell, Ernest, B.A., B.Sc., Dept. of Education, Box 33A, G.P.O., Sydney.
1891		Brennand, Henry J. W., B.A., M.D., Ch.M. *Syd.*, V.D., Surgeon Commander R.A.N. Ret., 223 Macquarie-street; p.r. 73 Milsons-road, Cremorne.
1919	P 1	Briggs, George Henry, B.Sc., Ph.D., Assistant-Professor of Physics in the University of Sydney.
1923		Brown, Herbert, "Sikoti," Alexander-street, Collaroy Beach, Sydney.
1906		Brown, James B., St. Andrew's, No. 1 Maitland-avenue, East Kew, E.4, Victoria.
1913	P 19	Browne, William Rowan, D.Sc., Assistant-Professor of Geology in the University of Sydney. (President.)
1898		‡Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. *Syd.*, "Wyoming," 175 Macquarie-street, Sydney.
1926		Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.
1919	P 10	Burrows, George Joseph, B.Sc., Lecturer and Demonstrator in Chemistry in the University of Sydney; p.r. Watson-street, Neutral Bay.

Elected.		
1929		Caley, Gilbert Fatkin, Manager, Glycerine Distillery Co., Ltd., Alexandria; p.r. "Windyridge," Park-road, Auburn.
1929	P 1	Callaghan, Allan Robert, D.Phil., B.Sc. *Oxon.*, Principal, Roseworthy Agricultural College, Adelaide, S.A.
1909		Calvert, Thomas Copley, Assoc.M.Inst.C.E., c/o Dept. of Public Works, Newcastle, N.S.W.
1923		Cameron, Lindsay Duncan, Hilly-street, Mortlake.
1891		Carment, David, F.I.A. *Grt. Brit. and Irel.*, F.F.A. *Scot.*, 4 Whaling-road, North Sydney.
1903	P 3	Carslaw, Horatio S., M.A., Sc.D., Professor of Mathematics in the University of Sydney.
1913	P 3	Challinor, Richard Westman, F.I.C., F.C.S., Lecturer in Chemistry, Sydney Technical College; p.r. 53 Drumalbyn-road, Bellevue Hill.
1909	P 2	Chapman, Henry G., M.D., B.S., Director of Cancer Research, University of Sydney. (Hon. Treasurer.)
1913	P 19	Cheel, Edwin, Curator, National Herbarium, Botanic Gardens, Sydney. (Vice-President.) (President, 1931.)
1925	P 1	Clark, William E., High School, Armidale.
1920		Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.
1913	P 4	Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College; p.r. Bannerman-crescent, Rosebery.
1928		Coppleson, Victor Marcus, M.B., Ch.M., F.R.C.S., 225 Macquarie-street, Sydney.
1882		Cornwell, Samuel, J.P., "Capanesk," Tyagarah, North Coast.
1919		Cotton, Frank Stanley, M.Sc., Chief Lecturer and Demonstrator in Physiology in the University of Sydney.
1909	P 7	Cotton, Leo Arthur, M.A., D.Sc., Professor of Geology in the University of Sydney. (Vice-President.) (President, 1929.)
1892	P 1	Cowdery, George R., Assoc.M.Inst.C.E., Strathfield-avenue, Strathfield.
1886		Crago, W. H., M.R.C.S. *Eng.*, L.R.C.P. *Lond.*, 135 Macquarie-street.
1921	P 1	‡Cresswick, John Arthur, 101 Villiers-street, Rockdale.
1925		Curry, Harris Eric Marshall, 89 Ridge-street, North Sydney.
1912		Curtis, Major Louis Albert, L.S., F.I.S. *N.S.W.*, V.D., Room 618, Government Savings Bank Building, Castlereagh-street; p.r. No. 1 Mayfair Flats, Macleay-street, Darlinghurst.
1890		Dare, Henry Harvey, M.E., M.Inst.C.E., Commissioner, Water Conservation and Irrigation Commission, Department of Agriculture Building, Raphael-street, Sydney.
1886	P 23	David, Sir Edgeworth, K.B.E., C.M.G., D.S.O., B.A., D.Sc., F.R.S., F.G.S., Wollaston Medallist, Emeritus Professor of Geology and Physical Geography in the University of Sydney; p.r. "Coringah," Burdett-street, Hornsby. (President, 1895, 1910.)

Elected.		
1928		Davidson, Walter Charles, General Manager, Clyde Engineering Company, Granville.
1930		Davies, Harold Whitridge, M.B., B.S. *Adel.*, Professor of Physiology in the University of Sydney.
1919	P 2	de Beuzeville, Wilfrid Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft, N.S.W.
1921		Delprat, Guillaume Daniel, C.B.E., "Keynsham," Mandeville-crescent, Toorak, Victoria.
1894		Dick, James Adam, C.M.G., B.A. *Syd.*, M.D., Ch.M., F.R.C.S. *Edin.*, "Catfoss," 59 Belmore-road, Randwick.
1906		‡Dixson, William, "Merridong," Gordon-road, Killara.
1913	P 3	Doherty, William M., F.I.C., F.C.S., Atlas Building, 8 Spring-street, Sydney; p.r. "Jesmond," George-street, Marrickville.
1928		Donegan, Henry Arthur James, A.S.T.C., Chemical Laboratory, Department of Mines, Sydney.
1908	P 6	Dun, William S., Palæontologist, Department of Mines, Sydney. (President, 1918.)
1924		Dupain, George Zephirin, A.A.C.I., F.C.S., Dupain Institute of Physical Education, Manning Building, Pitt and Hay-streets, Sydney; p.r. "Rose Bank," 158 Parramatta-road, Ashfield.
1924		Durham, Joseph, 120 Belmore-road, Randwick.
1923	P 11	Earl, John Campbell, D.Sc., Ph.D., Professor of Organic Chemistry in the University of Sydney.
1919		Earp, The Hon. George Frederick, C.B.E., M.L.C., Australia House, 52 Carrington-street.
1924		Eastaugh, Frederick Alldis, A.R.S.M., F.I.C., Associate Professor in Chemistry, Assaying and Metallurgy in the University of Sydney.
1916	P 2	Enright, Walter J., B.A., High-street, West Maitland, N.S.W.
1908		Esdaile, Edward William, 42 Hunter-street.
1921		Farnsworth, Henry Gordon, "Rothsay," 90 Alt-street, Ashfield.
1910		Farrell, John, A.T.C. *Syd.*, Riverina Flats, 265 Palmer-street, Sydney.
1909	P 7	Fawsitt, Charles Edward, D.Sc., Ph.D., Professor of Chemistry in the University of Sydney. (President, 1919.)
1922		Ferguson, Andrew, B.Sc., 22 Village Lower-rd., Vaucluse.
1927	P 3	Finnemore, Horace, B.Sc., F.I.C., Lecturer in Pharmacy in the University of Sydney.
1923		Fiaschi, Piero, O.B.E., M.D. *Columbia Univ.*, D.D.S. *New York*, M.R.C.S. *Eng.*, L.R.C.P. *Lond.*, 178 Phillip-street.
1920		Fisk, Ernest Thomas, Wireless House, 47 York-street.
1888		Fitzhardinge, His Honour Judge G. H., M.A., "Red Hill," Pennant Hills.
1879		‡Foreman, Joseph, M.R.C.S. *Eng.*, L.R.C.P. *Edin.*, "The Astor," Macquarie-street.

Elected.		
1932		Forman, Kenn. P., Refrigeration Engineer, Electricity Meter Mfg. Co., Ltd., Waterloo; p.r. "Shelford," Willis-street, South Kensington.
1920		Fortescue, Albert John, "Benambra," Loftus-street, Arncliffe.
1905		Foy, Mark, c/o Hydro Office, Liverpool and Elizabeth-streets, Sydney.
1925		Friend, Norman Bartlett, 48 Pile-street, Dulwich Hill.
1918		Gallagher, James Laurence, M.A. *Syd.*, "Akaroa," Ellesmere-avenue, Hunter's Hill.
1926		Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E. *Aust.*, 906 Culwulla Chambers, Castlereagh-street, Sydney.
1921		Godfrey, Gordon Hay, M.A., B.Sc., Lecturer in Physics in the Technical College, Sydney; p.r. "Eversham," Victoria-parade, Manly.
1897		Gould, The Hon. Sir Albert John, K.B., V.D., "Eynesbury," Edgecliff.
1932		Goulder, Francis, A.S.T.C., A.A.C.I., Manager, Ever-Ready Works, Marshall-street, Surry Hills, Sydney.
1922	P 2	Greig, William Arthur, Mines Department, Sydney.
1923		Gurney, William Butler, B.Sc., F.E.S., Government Entomologist, Department of Agriculture, Sydney.
1880	P 5	Halligan, Gerald H., L.S., F.G.S., "Geraldine," Culworth-avenue, Killara.
1912		Hallmann, E. F., B.Sc., 72 John-street, Petersham.
1892		Halloran, Henry Ferdinand, L.S., 82 Pitt-street.
1919		Hambridge, Frank, Adelaide Steamship Co. Chambers, 22 Bridge-street, Sydney.
1912		Hamilton, Alexander G., "Tanandra," Hercules-street, Chatswood.
1909		Hammond, Walter L., B.Sc., High School, Bathurst.
1905	P 5	Harker, George, D.Sc., F.A.C.I., 57 Junction-street, Summer Hill.
1913	P 1	Harper, Leslie F., F.G.S., Geological Surveyor, Department of Mines, Sydney.
1923	P 1	Harrison, Travis Henry, B.Sc.Agr., Lecturer in Botany and Entomology at the Hawkesbury Agricultural College, Richmond; p.r. c/o F. W. Holliday, Grand View-parade, Epping.
1918		Hassan, Alex. Richard Roby.
1929		Hawley, Joseph William, 15 Springdale-road, Killara.
1914		Hector, Alex. Burnet, "Druminard," Greenwich-road, Greenwich.
1916		Henderson, James, "Dunsfold," Clanalpine-street, Mosman.
1919		Henriques, Frederick Lester, 208 Clarence-street.
1919	P 2	Henry, Max, D.S.O., B.V.Sc., M.R.C.V.S., Chief Veterinary Surgeon, Dept. Agriculture, Sydney; p.r. "Coram Cottage," Essex-street, Epping.
1918		Hindmarsh, Percival, M.A., B.Sc.Agr., Teachers' College, The University, Sydney; p.r. "Lurnea," Canberra-avenue, Greenwich.

Elected.		
1921	P 2	Hindmarsh, William Lloyd, B.V.Sc., M.R.C.V.S., D.V.H., District Veterinary Officer, Glenfield.
1928		Hirst, George Walter Cansdell, B.Sc., Power and Mechanical Branch, Department of Transport for N.S.W., Wilson-street, Redfern; p.r. "St. Cload," Beaconsfield-road, Chatswood.
1930		Hodson, John S., Electrical Engineer, H.M. Naval Establishments, Garden Island, Sydney.
1916		Hoggan, Henry James, A.M.I.M.E., A.M.I.E. *Aust.*; p.r. "Lincluden," Frederick-street, Rockdale.
1924		Holme, Ernest Rudolph, O.B.E., M.A., Professor of English Language in the University of Sydney.
1930		Holmes, James MacDonald, Associate Professor of Geography in the University of Sydney.
1901		Holt, Thomas S., "Amalfi," Appian Way, Burwood.
1905	P 3	Hooper, George, J.P., F.S.T.C. *Syd.*, "Mycumbene," Nielsen Park, Vaucluse.
1919		Hoskins, Arthur Sidney, Eskroy Park, Bowenfels.
1919		Hoskins, Cecil Harold, c/o Australian Iron and Steel Co., Ltd., Kembla Building, Margaret-street, Sydney.
1913		Hudson, G. Inglis, J.P., F.C.S., 55 Wunulla-road, Woollahra Point.
1923	P 2	‡Hynes, Harold John, M.Sc., B.Sc.Agr., Senior Asst. Biologist, Department of Agriculture, Sydney.
1922		Jacobs, Ernest Godfried, "Cambria," 106 Bland-street, Ashfield.
1904		Jaquet, John Blockley, A.R.S.M., F.G.S., 6 Treatt's-road, Lindfield.
1929		Jeffrey, Robert Ewen, A.A.C.I., Managing Director, Bardsley's Ltd.; p.r. 9 Greycliffe-avenue, Vaucluse.
1925		Jenkins, Charles Adrian, B.E., B.Sc., 2 Ramsgate-avenue, Bondi Beach.
1917		Jenkins, Richard Ford, Engineer for Boring, Irrigation Commission, 6 Union-street, Mosman.
1918		John, Morgan Jones, M.I.Mech.E., A.M.I.E.E. *Lond.*, M.I.E. *Aust.*, M.I.M. *Aust.*; p.r. Village High-road, Vaucluse.
1909	P 15	Johnston, Thomas Harvey, M.A., D.Sc., F.L.S., C.M.Z.S., Professor of Zoology in the University of Adelaide.
1924		Jones, Leo Joseph, Geological Surveyor, Department of Mines, Sydney.
1930		Judd, William Percy, 49 Hirst-street, Arncliffe.
1911		Julius, Sir George A., Kt., B.Sc., M.E., M.I.Mech.E., Culwulla Chambers, Castlereagh-street, Sydney.
1932		Keeble, Arthur Thomas, B.Sc., Science Master, Sydney Grammar School; p.r. 55 Carlotta-street, Greenwich.
1924		Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 5 Savings Bank Flats, Bondi Beach.
1887		Kent, Harry C., M.A., F.R.I.B.A., 35 Beresford-road, Rose Bay.
1919	P 3	Kesteven, Hereward Leighton, M.D., Ch.M., D.Sc., Bullahdelah, N.S.W.

Elected.		
1896		King, Sir Kelso, K.B., Mercantile Mutual Building, 117 Pitt-street, Sydney.
1923		Kinghorn, James Roy, Australian Museum, Sydney.
1920		Kirchner, William John, B.Sc., "Wanawong," 27 Thornleigh-road, Beecroft.
1919		Kirk, Robert Newby, 25 O'Connell-street.
1877		Knox, Edward W., "Rona," Bellevue Hill, Double Bay.
1932		Lane, Ralph Charles Bradley, M.A., B.Sc. *Melb.*, A.M.P. Society, 87 Pitt-street, Sydney.
1924		Leech, Thomas David James, B.Sc. *Syd.*, "Orontes," Clarke-street, Granville.
1920		Le Souef, Albert Sherbourne, Taronga Park, Mosman.
1916		L'Estrange, Walter William, 7 Church-street, Ashfield.
1909		Leverrier, Frank, B.A., B.Sc., K.C., Wentworth-road, Vaucluse.
1883		Lingen, J. T., M.A. *Cantab.*, K.C., c/o Union Club, Bligh-street.
1929	P 9	Lions, Francis, B.Sc., Ph.D., Lecturer in Organic Chemistry in the University of Sydney; p.r. 21 Bridge-street, Epping.
1906		Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street.
1924		Love, David Horace, Beauchamp-avenue, Chatswood.
1927	P 1	Love, William Henry, B.Sc., Ph.D., Cancer Research Department, University of Sydney.
1884		MacCormick, Sir Alexander, K.C.M.G., M.D., C.M. *Edin.*, M.R.C.S. *Eng.*, 185 Macquarie-street.
1930		MacKenzie, William Donald, M.I.Chem.E., A.I.C., Technical Director, Messrs. Lever Bros., Ltd., Balmain; p.r. 5 Tivoli-avenue, Rose Bay.
1921		McDonald, Alexander Hugh Earle, Director of Agriculture, Department of Agriculture, Sydney.
1903		McDonald, Robert, J.P., L.S., Pastoral Chambers, O'Connell-street; p.r. "Lowlands," William-street, Double Bay.
1919		McGeachie, Duncan, M.I.M.E., M.I.E. *Aust.*, M.I.M.M. *Aust.*, "Craig Royston," Toronto, Lake Macquarie.
1906	P 2	McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville.
1891		McKay, R. T., L.S., M.Inst.C.E., Commissioner, Sydney Harbour Trust, Circular Quay.
1932		McKie, Rev. Ernest Norman, B.A. *Syd.*, The Manse, Guyra, N.S.W.
1927		McMaster, Frederick Duncan, "Dalkeith," Cassilis.
1916		McQuiggin, Harold G., M.B., Ch.M., B.Sc., Lecturer and Demonstrator in Physiology in the University of Sydney; p.r. "Berolyn," Beaufort-street, Croydon.
1909		Madsen, John Percival Vissing, D.Sc., B.E., Professor of Electrical Engineering in the University of Sydney.

Elected.		
1924		Mance, Frederick Stapleton, Under Secretary for Mines, Mines Department, Sydney; p.r. "Binbah," Lucretia-avenue, Longueville.
1880	P 1	Manfred, Edmund C., Belmore-square, Goulburn.
1920	P 1	Mann, Cecil William, 41 Jenkin-street, Chatswood.
1920		Mann, James Elliott Furneaux, Barrister-at-Law, c/o T. H. Southerden, Esq., Box 1646JJ, G.P.O., Sydney.
1914		Martin, A. H., Technical College, Sydney.
1929	P 1	Matheson, Alexander James, Teacher, The High School, Dubbo.
1926		Mathews, Hamilton Bartlett, B.A. *Syd.*, Surveyor-General of N.S.W., Department of Lands, Sydney.
1912		Meldrum, Henry John B.A., B.Sc., "Craig Roy," Sydney-road, Manly.
1929	P 3	Mellor, David Paver, Assistant Lecturer in Inorganic Chemistry in the Universtiy of Sydney; p.r. Flat 8, "Deanville," Milson-road, Cremorne.
1928		Micheli, Louis Ivan, Ph.D., Colonial Sugar Refining Co., Pyrmont.
1926		Mitchell, Ernest Marklow, 106 Harrow-road, Rockdale.
1879		Moore, Frederick H., Union Club, Sydney.
1931	P 1	Moppett, Warnford, M.D., Ch.M., Cancer Research Department, University of Sydney.
1922	P 18	Morrison, Frank Richard, A.A.C.I., F.C.S., Assistant Chemist, Technological Museum, Sydney; p.r. Brae-street, Waverley.
1924		Morrison, Malcolm, Department of Mines, Sydney.
1879		Mullins, John Lane, M.L.C., M.A. *Syd.*, "Mount Stewart," Edgecliff-road, Edgecliff.
1932		Munch-Petersen, Erik, M.Sc., Ph.B., Analytical Chemist, 31 Lytton-street, North Sydney.
1915		Murphy, R. K., Dr.Ing., Chem.Eng., Lecturer in Chemistry, Technical College, Sydney.
1923	P 2	Murray, Jack Keith, B.A., B.Sc.Agr., Principal, Queensland Agricultural College, Gatton, Queensland.
1893	P 4	Nangle, James, O.B.E., F.R.A.S., Superintendent of Technical Education, The Technical College, Sydney; Government Astronomer, The Observatory, Sydney. (President, 1920.)
1930	P 1	Naylor, George Francis King, "Kingsleigh," Ingleburn, N.S.W.
1932		Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., "Tip Tree," Kingsland-road, Strathfield.
1924		Nickoll, Harvey, L.R.C.P., L.R.C.S., Barham, *viâ* Mudgee, N.S.W.
1891		‡Noble, Edward George, L.S., 8 Louisa-road, Balmain.
1920	P 1	Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Biologist, Dept. of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Casa Loma," Shell Cove-road, Neutral Bay. (Hon. Secretary.)
1903		‡Old, Richard, "Waverton," Bay-road, North Sydney.
1921		Olding, George Henry, "Werriwee," Wright's-road, Drummoyne.

Elected.		
1930		O'Leary, William, S.J., Seismologist, St. Ignatius' College, Riverview, Sydney.
1913		Ollé, A. D., F.C.S., "Kareema," Charlotte-street, Ashfield.
1932		O'Neill, John Patrick, S.F.A.I., Chief Timber Inspector, Department of Transport, N.S.W., Transport Office, Bridge-street, Sydney; p.r. 38 Wilberforce-avenue, Rose Bay.
1928		Osborn, Theodore George Bentley, D.Sc., F.L.S., Professor of Botany in the University of Sydney.
1921	P 3	Osborne, George Davenport, D.Sc., Lecturer and Demonstrator in Geology in the University of Sydney.
1921	P 1	Parkes, Varney, Conjola, South Coast.
1928		Parsons, Stanley William Enos, Analyst and Inspector, N.S.W. Explosive Department; p.r. Shepherd-road, Artarmon.
1920	P 60	Penfold, Arthur Ramon, F.C.S., Curator and Economic Chemist, Technological Museum, Harris-street, Ultimo.
1881		Poate, Frederick, F.R.A.S., L.S., "Clanfield," 50 Penkivil-street, Bondi.
1919		Poate, Hugh Raymond Guy, M.B., Ch.M. *Syd.*, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, 225 Macquarie-street.
1896		Pope, Roland James, B.A. *Syd.*, M.D., Ch.M., F.R.C.S. *Edin.*, 185 Macquarie-street.
1921	P 2	Powell, Charles Wilfrid Roberts A.I.C., c/o Colonial Sugar Refining Co., O'Connell-street.
1918		Powell, John, 17 Thurlow-street, Redfern.
1927		Price, William Lindsay, B.E., B.Sc., 60 McIntosh-street, Gordon.
1918		Priestley, Henry, M.D., Ch.M., B.Sc., Associate-Professor of Physiology in the University of Sydney.
1893		Purser, Cecil, B.A., M.B., Ch.M. *Syd.*, 185 Macquarie-street.
1929		Pyke, Henry George, Chemical Testing Assistant, N.S.W. Government Tramways; p.r. Bellamy-street, Pennant Hills.
1927		Radcliffe-Brown, Alfred Reginald, M.A. *Cantab.*, M.A. *Adel.*, F.R.A.I. *Cantab.*, c/o Department of Anthropology, University of Chicago, Chicago, Illinois, U.S.A.
1922	P 5	Raggatt, Harold George, M.Sc., "Meru," Epping-avenue, Epping.
1919	P 3	Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., Lecturer in Physics, Teachers' College, The University, Sydney.
1931		Rayner, Jack Maxwell, B.Sc., A.Inst.P., Physicist to the Department of Mines, Sydney; p.r. 125 William-street, Granville.
1928		Reidy, Eugene Nicholas, A.S.T.C., Analyst, Department of Mines, Sydney.
1932		Richardson, Henry Elmar, Chemist, Chase-road, Turramurra.

Elected.			
1928			Ross, Allan Clunies, B.Sc., 13 Bond-street, Sydney. (Member from 1915 to 1924.)
1884	P	1	Ross, Chisholm, M.D. *Syd.*, M.B., Ch.M. *Edin.*, 225 Macquarie-street.
1895			Ross, Herbert E., Govt. Savings Bank Building, 14 Castlereagh-street, Sydney.
1925			Roughley, Theodore Cleveland, Zoologist, Technological Museum, Sydney.
1929			Royle, Norman Dawson, M.D., Ch.M., 185 Macquarie-street, Sydney.
1907			Ryder, Charles Dudley, D.Eng. *Vienna*, Assoc.I.R.S.M. *Lond.*, Assoc.A.C.I., F.C.S. *Lond.*, Public Analyst (by appointment), 38 Copeland-street, Beecroft.
1922			Sandy, Harold Arthur Montague, 268 George-street.
1920			Sawyer, Basil, B.E., "Birri Birra," The Crescent, Vaucluse.
1920			Scammell, Rupert Boswood, B.Sc. *Syd.*, "Storrington," 10 Buena Vista-avenue, Clifton Gardens.
1923	P	1	Seddon, Herbert Robert, D.V.Sc., Director, Veterinary Research Station, Glenfield.
1918			Sevier, Harry Brown, c/o Lewis Berger and Sons (Aust.), Ltd., Cathcart House, Castlereagh-street.
1924			Shelton, James Peel, M.Sc., B.Sc.Agr., 16 Holland-road, Bellevue Hill.
1927			Shearsby, Alfred James, c/o H. C. Whibley, 18 Boomerang-street, Haberfield.
1917			Sibley, Samuel Edward, Mount-street, Coogee.
1900			‡Simpson, R. C., Lecturer in Electrical Engineering, Technical College, Sydney.
1922	P	1	Smith, Thomas Hodge, Australian Museum, Sydney.
1919			Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
1921			Spencer-Watts, Arthur, "Araboonoo," Glebe-street, Randwick.
1917			Spruson, Wilfred Joseph, S.M. Herald Building, Pitt and Hunter-streets, Sydney.
1916			Stephen, Alfred Ernest, F.C.S., c/o Box 1158HH., G.P.O., Sydney.
1921			Stephen, Henry Montague, B.A., LL.B., c/o Messrs. Maxwell and Boyd, 17 O'Connell-street.
1914			Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., Captain Piper's-road and New South Head-road, Vaucluse.
1920	P	1	Stephens, John Gower, M.B., 135 Macquarie-street, Sydney.
1913			Stewart, Alex. Hay, B.E., "Yunah," 22 Murray-street, Croydon.
1900	P	1	Stewart, J. Douglas, B.V.Sc., M.R.C.V.S., Professor of Veterinary Science in the University of Sydney ; p.r. "Berelle," Homebush-road, Strathfield. (Vice-President.) (President, 1927.)
1909			Stokes, Edward Sutherland, M.B. *Syd.*, F.R.C.P. *Irel.*, Medical Officer, Metropolitan Board of Water Supply and Sewerage, 341 Pitt-street.

Elected.		
1916	P 1	Stone, W. G., Assistant Analyst, Department of Mines, Sydney.
1920		Sulman, Sir John, KT., Warrung-street, McMahon's Point, North Sydney.
1918		Sundstrom, Carl Gustaf, c/o Federal Match Co., Park-road, Alexandria.
1901	P 14	‡Sussmilch, C. A., F.G.S., F.S.T.C., A.M.I.E. *Aust.*, Principal of the East Sydney Technical College, and Assistant Superintendent of Technical Education. (President, 1922.) (Hon. Secretary.)
1919		‡Sutherland, George Fife, A.R.C.Sc. *Lond.*, Assistant Professor in Mechanical Engineering in the University of Sydney.
1920		Sutton, Harvey, O.B.E., M.D., D.P.H. *Melb.*, B.Sc. *Oxon.*; p.r. "Lynton," Kent-road, Rose Bay. Professor of Preventive Medicine and Director, Commonwealth Health Dept., University of Sydney.
1926		Tannahill, Robert William, B.Sc. *Syd.*, M.Sc., "Eastwell," 40 Cammaray-avenue, North Sydney.
1915	P 3	Taylor, Harold B., D.Sc., Kenneth-street, Longueville.
1905		‡Taylor, John M., M.A., LL.B. *Syd.*, "Woonona," 43 East Crescent-street, McMahon's Point, North Sydney.
1923		Thomas, David, B.E., M.I.M.M., F.G.S., 12 Clifton-avenue, Burwood.
1919		Thorne, Harold Henry, B.A. *Cantab.*, B.Sc. *Syd.*, Lecturer in Mathematics in the University of Sydney; p.r. 96 Rutledge-street, Eastwood.
1916		Tillyard, Robin John, M.A., D.Sc., F.R.S., F.L.S., F.E.S., Chief Commonwealth Entomologist, G.P.O. Box 109, Canberra, F.C.T.
1923		Tindale, Harold, Works Engineer, c/o Australian Gas-Light Co., Mortlake.
1923		Toppin, Richmond Douglas, A.I.C., Box 1454JJ, G.P.O., Sydney.
1879		Trebeck, P. C., c/o Box 367F, G.P.O., Sydney; p.r. No. 4 Chesterton Flats, Carabella-street, Kirribilli.
1932	P 6	Trikojus, Victor Martin, B.Sc., D.Phil., Lecturer in Inorganic Chemistry, University of Sydney, Sydney.
1925		Tye, Cyrus Willmott Oberon, Director of Development and of the Migration Agreement Executive Committee, Public Works Dept. Building, Sydney; p.r. 19 Muston-street, Mosman.
1890		Vicars, James, M.E., Memb. Intern. Assoc. Testing Materials, Memb. B.S. Guild., Challis House, Martin Place.
1921		Vicars, Robert, Marrickville Woollen Mills, Marrickville.
1892		Vickery, George B., 9th Floor, Barrack House, Barrack-street, Sydney.
1903	P 7	Vonwiller, Oscar U., B.Sc., F.Inst.P., Professor of Physics in the University of Sydney. (Vice-President.) (President, 1930.)

Elected.		
1910		Walker, Charles, "Lynwood," Terry-road, Ryde.
1910		Walker, Harold Hutchison, Vickery's Chambers, Box 1723JJ, G.P.O., Sydney, 82 Pitt-street.
1879		Walker, H. O., "Moora," Crown-street, Granville.
1919	P 1	Walkom, Arthur Bache, D.Sc., Science House, Gloucester and Essex-streets.
1903		Walsh, Fred., J.P., Consul-General for Honduras in Australia and New Zealand; For. Memb. Inst. Patent Agents, London; Patent Attorney Regd. U.S.A.; Memb. Patent Law Assoc., Washington; Regd. Patent Attorn. Comm. of Aust.; Memb. Patent Attorney Exam. Board Aust.; 4th Floor, 16 Barrack House, Barrack-street, Sydney; p.r. "Walsholme," Centennial Park, Sydney.
1901		Walton, R. H., F.C.S., "Flinders," Martin's-avenue, Bondi.
1913	P 4	Wardlaw, Hy. Sloane Halcro, D.Sc. *Syd.*, Lecturer and Demonstrator in Physiology in the University of Sydney.
1922		Wark, Blair Anderson, V.C., D.S.O., M.I.Q.C., c/o Thompson and Wark, T. & G. Building, Elizabeth-street; p.r. "Braeside," Zeta-street, Lane Cove, Sydney.
1921		‡Waterhouse, G. Athol, D.Sc., B.E., F.E.S., 39 Stanhope-road, Killara.
1924		Waterhouse, Leslie Vickery, B.E. *Syd.*, 6th Floor, Wingello House, Angel Place, Sydney.
1919		Waterhouse, Lionel Lawry, B.E. *Syd.*, Lecturer and Demonstrator in Geology in the University of Sydney.
1919	P 3	Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., "Hazelmere," Chelmsford-avenue, Roseville.
1910		Watson, James Frederick, M.B., Ch.M., Canberra, F.C.T.
1911	P 1	Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney. (President, 1925.) (Vice-President.)
1920	P 32	Welch, Marcus Baldwin, B.Sc., A.I.C., Economic Botanist, Technological Museum.
1920	P 1	Wellish, Edward Montague, M.A., Associate-Professor in Mathematics in the University of Sydney.
1921		Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding Department of Agriculture, Sydney.
1881		‡Wesley, W. H., London.
1931		Wheatley, Frederick William, C.B.E., 73 Darling Point-road, Darling Point.
1922		Whibley, Harry Clement, 18 Boomerang-street, Haberfield.
1909	P 3	‡White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teacher's College.
1928		Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., 143 Macquarie-street, Sydney.
1921		Willan, Thomas Lindsay, B.Sc., Ipoh, Berak, Federated Malay States.
1920		Williams, Harry, A.I.C., c/o Whiddon Bros.' Rosebery Lanolines Pty. Ltd., Arlington Mills, Botany.
1891		Wood, Percy Moore, L.R.C.P. *Lond.*, M.R.C.S. *Eng.*, "Redcliffe," Liverpool-road, Ashfield.

Elected.		
1906	P 11	Woolnough, Walter George, D.Sc., F.G.S., "Callabonna," Park-avenue, Gordon. (President, 1926.)
1916		Wright, George, c/o Farmer & Company, Pitt-street.
1917		Wright, Gilbert, Lecturer and Demonstrator in Agricultural Chemistry in the University of Sydney.
1921		Yates, Guy Carrington, 184 Sussex-street.

Honorary Members.

Limited to Twenty.

M.—Recipients of the Clarke Medal.

Elected.		
1914		Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, London.
1931		Lyle, Sir Thomas Ranken, K.B., C.B.E., M.A., D.Sc., F.R.S., "Lisbuoy," Irving-road, Toorak, Melbourne.
1915		Maitland, Andrew Gibb, F.G.S., ex-Government Geologist of Western Australia, "Bon Accord," 28 Melville Terrace, South Perth, W.A.
1912		Martin, C. J., C.M.G., D.Sc., F.R.S., Director of Animal Nutrition, C.S. and I.R., University of Adelaide.
1930		Masson, Sir David Orme, K.B.E., M.A., D.Sc., LL.D., 14 William-street, South Yarra, Victoria.
1928		Smith, Grafton Elliott, M.A., M.D., F.R.S., F.R.C.P., Professor of Anatomy in the University College, London.
1915		Thomson, Sir J. J., O.M., D.Sc., F.R.S., Nobel Laureate, Master of Trinity College, Cambridge, England.
1922		Wilson, James T., M.B., Ch.M. *Edin.*, F.R.S., Professor of Anatomy in the University of Cambridge, England, 31 Grange-road, Cambridge, England.

Obituary 1932-33.

Ordinary Members.

1923 Brereton, Ernest Le Gay
1920 Carruthers, Joseph Hector
1924 Robertson, James R. M.
1876 Watkins, John Leo

Honorary Members.

1908 Kennedy, Alex. B. W.
1921 Threlfall, Richard

AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

Vice-President from 1866 to 1878.

To be awarded from time to time for meritorious contributions to the Geology, Mineralogy, or Natural History of Australia. The prefix * indicates the decease of the recipient.

Awarded.

1878 *Professor Sir Richard Owen, K.C.B., F.R.S.
1879 *George Bentham, C.M.G., F.R.S.
1880 *Professor Thos. Huxley, F.R.S.
1881 *Professor F. M'Coy, F.R.S., F.G.S.
1882 *Professor James Dwight Dana, LL.D.
1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.
1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
1886 *Professor L. G. De Koninck, M.D.
1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.
1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.
1893 *Professor Ralph Tate, F.L.S., F.G.S.
1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
1895 *Robert Etheridge, Jnr.
1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
1900 *Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.
1901 *Edward John Eyre.
1902 *F. Manson Bailey, C.M.G., F.L.S.
1903 *Alfred William Howitt, D.Sc., F.G.S.
1907 Walter Howchin, F.G.S., University of Adelaide.
1909 Dr. Walter E. Roth, B.A., Pomeroon River, British Guiana, South America.
1912 *W. H. Twelvetrees, F.G.S.
1914 A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
1915 *Professor W. A. Haswell, M.A., D.Sc., F.R.S.
1917 Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., B.A., D.Sc., F.R.S., F.G.S., The University, Sydney.
1918 Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
1920 *Joseph Edmund Carne, F.G.S.
1921 *Joseph James Fletcher, M.A., B.Sc.
1922 Richard Thomas Baker, The Crescent, Cheltenham.
1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
1925 *Charles Hedley, F.L.S.
1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
1928 Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.

1929 Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.

1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.

1931 Robin John Tillyard, M.A., D.Sc., F.R.S., F.L.S., F.E.S., Chief Commonwealth Entomologist, Canberra, F.C.T.

1932 Frederick Chapman, A.L.S., F.G.S., National Museum, Melbourne.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.

1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."

1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal and £25.

1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."

1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."

1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."

1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."

1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."

1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."

1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."

1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."

1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."

1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."

1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."

1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."

AWARDS OF THE WALTER BURFITT PRIZE.

MONEY AND MEDAL.

Money Prize of £50.

Established as the result of a generous gift to the Society by Dr. W. F. Burfitt, B.A., M.B., Ch.M., B.Sc., of Sydney. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past three years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.

1932 Charles Halliby Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (This Journal, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.

VOL. LXVI. PART I.

JOURNAL
AND
PROCEEDINGS
OF THE
ROYAL SOCIETY
OF
NEW SOUTH WALES
FOR
1932
(INCORPORATED 1881)

PART I (pp. 1 to 180)
OF
VOL. LXVI

Containing Presidential Address and Papers
Read in June, with One Plate.
(Plate I)

EDITED BY
THE HONORARY SECRETARIES.

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN.

SYDNEY
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GLOUCESTER AND ESSEX STREETS

1932

CONTENTS.

VOLUME LXVI.

Part I.

PRESIDENTIAL ADDRESS

By Edwin Cheel,
Curator, National Herbarium, Botanic Gardens, Sydney.

(Delivered to the Royal Society of New South Wales, May 4, 1932.)

Part I.

Introduction.

Gentlemen, in following the custom established by many Past Presidents of this Society, I feel that it will not be out of place for me to give a brief outlined summary of the advances made in connection with science and to report on the progress or otherwise of matters closely associated with the well-being of the Royal Society of New South Wales, and which also more or less affects kindred organisations in this State. Notwithstanding the unparalleled depression which has obtained during the whole tenure of my occupancy of the position as President of this Society, I am pleased to be able to state that the objects of the Society, as outlined in the first volume of our Journal and Proceedings, published in 1867, "to receive original papers on subjects as tend to develop the resources of Australia and to illustrate its natural history and production", have been well maintained. The present circumstances of depression do not in any way diminish the great national resources of Australia nor throw any doubt upon the possibilities of the future development in what we hope in the very near future will be happier and more prosperous days. The willing worker will find abundant material close at hand to

which he may devote his spare moments and from which he may derive the training he seeks. Science will be the gainer by the facts discovered and arranged; the worker will be the gainer by the training and experience. Science plays so many and such diverse parts in directing, welding and ameliorating the daily life of the people that it is worthy of the most liberal support.

Without science as its foundation, the Commonwealth cannot hope to keep a place among the nations of the world. With the aid of science its possibilities may become unbounded. The power to promote a greater interest in scientific affairs lies in the hands of the people who elect those in charge of our governmental affairs. The community can only be guided into the safety zones leading to prosperity by those who have a deep sense of responsibility and who can fully appreciate the closeness of the touch of science, and that industry, manufacturing, medicine, health and public safety, largely depend for their advance on the work of research laboratories. It is probably owing to the lack of this knowledge on the part of those in control, that this and other countries are unable to solve the deplorable social menace of unemployment. We need a more harmonious and progressive development of the scientific services than is at present practicable with the existing departmental structure.

It is stated that in Great Britain there is a turnover of £40,000,000 worth of horticultural produce annually. About £25,000,000 worth of this is imported from other countries. It would be of special interest to know just how much value could be placed on the turnover of horticultural products located in the six cities of the Commonwealth of Australia. The economics of these

products in Australia should be as much the concern of scientists as are matters of other branches of scientific investigations, because of the much more varied character of our fruits, flowers and vegetables, and because of the diseases and pests which affect these crop plants. It is considered also that well-tilled cottage garden allotments or orchards would have a moral effect on the vast number of unemployed persons if their attention was directed more closely to this form of primary production. There is no doubt that secondary industries would be established as a result of more intensive cultivation of smaller plots of land, if proper methods were utilised for preserving surplus products derived therefrom.

There is, to a certain extent, an indifference towards science. Even where material pecuniary profits are in prospect, the same objection is sometimes perceived. This indifference may be caused through the scientists themselves being at a loss to translate themselves and their work into simple words and terms. It is not always possible to do this, because of the lack of funds which are necessary for the purpose of publishing the results of the research work of specialists in plain language suitable for the average person. It may be true, as has frequently been stated, that "scientists write only for scientists", but it must always be remembered that the systematic botanists, like all other scientific workers, are compelled to keep in touch with the advances in all lines of research work. The specialist in any branch of scientific investigation rarely retains his grasp upon general work, because of his special duties which do not permit of sufficient time being devoted to the work which is being done in branches of investigation

other than that in which he is a specialist. It may be necessary to create a taste for things of scientific interest which may lead to higher pursuits. It is the initial desire of this Society and other scientific institutions to extend our knowledge of the vast reserves of natural products and, as far as possible, to investigate other fields with a view to making other discoveries which may reveal vast stores of hidden treasures. There are many persons in this community who could materially serve the objects of this Society, if they would only lay aside a want of confidence and apply themselves to review the accomplishments of the scientific institutions in the various States in their proper perspective.

It is a question of very great importance as to whether the public should be served up with lectures on scientific matters in a more popular fashion, or whether there should be a continuance of what is sometimes regarded as pedantic descriptive scientific jargon. Scientists themselves have to forage through reams of literature couched in languages of all nations, which must be translated for the purpose of a proper understanding of the subjects under discussion. The technique used in the discussion is common to all nations, and is published in the annales of scientific societies all over the world. All that is required is for the people themselves to relieve the strain of work, so that more time might be permitted for charting the facts concerning the vast stores of riches contained in the mineral, animal and vegetable kingdoms of the world. It does not require much intelligence to be convinced that our natural wealth of raw products must be the starting point in any industry, and that these subjects have a deep financial interest and are of

economic and social importance, and require the full support of all classes of people.

Taxes on Knowledge.

During the year scientists received a rude shock owing to the extra burden having been imposed on them in the form of a tax on knowledge. It is a well-known fact that the requirements of professional and technical experts are a special desideratum and can only be obtained by the united efforts of our universities, scientific institutions and state libraries. The cost of procuring such works is far beyond the pockets of the individual technical worker and scientist. It is for this reason that a small band of citizens who are seized with a full sense of their responsibilities as citizens, devote a large amount of their leisure moments to a study of the natural phenomena around them and take an active part in scientific research. It is only by the aid of literature that we are able to keep abreast of modern technical investigations of other countries. Heavy taxes have been imposed on works of scientific literature; prices of publications from Great Britain and foreign countries have been increased by 70 to 80 per cent. This is a most serious blow, and will have a detrimental effect upon the efficiency of the whole community because of the extremely heavy burden imposed on our universities, scientific institutions and public libraries, which are unable to find sufficient funds to meet these extra heavy demands. Public libraries and scientific institutions must, of necessity, discontinue their subscriptions to overseas institutions because of the exchange rates, primage and sales taxes. Efforts have been made to restore these tools of trade to those following scientific

avocations by a strong deputation representing practically the whole of the educational institutions of Australia. It was pointed out that technical books and journals published in Great Britain, Europe and America, which are indispensable to the medical, electrical or engineering student, have increased enormously in price, and, in certain instances, students have had to give up the purchase of them. These works cannot be published in Australia because the circulation here would not warrant the expenditure entailed.

Scientific Activities.

During the year there have been eight general monthly meetings, at which eighteen papers were read, and ten council meetings of the Society.

In addition to the papers, lecturettes were given by Professor C. E. Fawsitt, Ph.D., Dr. W. L. Waterhouse, M.C., Professor J. C. Earle, D.Sc., Ph.D., A. R. Penfold, F.A.C.I., F.C.S., Professor H. G. Chapman, and C. A. Sussmilch, F.G.S., and the Society is greatly indebted to these gentlemen for their kindness in this connection.

At the invitation of the Council the first Liversidge Lecture was delivered on Thursday, 24th September, 1931, by Mr. H. Hey, entitled: "The Production of Zinc by Electrolysis of Zinc Sulphate Solution."

Four popular lectures were also delivered as follows:

"Oysters and Oyster Culture", by T. C. Roughley.

"The Oceanographical Work of the 'S.Y. Discovery' in the Antarctic Seas", by W. W. Ingram, M.C., M.D., Ch.M.

"The Sun", by Rev. Wm. O'Leary, S.J.

"Insect Life", by W. B. Gurney, B.Sc.

The seventy-fifth anniversary of the Society was celebrated at the monthly meeting in October. Dr. H. G. Chapman gave a brief *résumé* of the active part which Sir William Denison, Governor of the State, had played in the foundation of the Society. Sir Edgeworth David gave an excellent account of the services rendered to the Society and to the Commonwealth of Australia by noted geologists. Dr. J. A. Dick explained to the members the work of the medical fraternity during the years 1876-1901. Mr. James Nangle gave an historical sketch of the work on astronomy, and Sir Henry Barraclough recounted the work of the engineering section.

The Michael Faraday Centenary Celebrations were conducted at the University of Sydney on the 22nd September, 1931, under the auspices of the Institution of Engineers of Australia (Sydney Division), the Institute of Electrical Engineers, London (N.S.W. Branch), the Institution of Civil Engineers, London (N.S.W. Branch), the Royal Society of New South Wales, and the Australian Chemical Institute (N.S.W. Branch).

The commemorative addresses were delivered by Professors O. U. Vonwiller and J. P. Madsen. Similar functions were conducted in Great Britain, and Dr. W. H. Love was appointed as a delegate to represent this Society.

The Centenary Meeting of the British Association for the Advancement of Science was held in London, and Professor Radcliffe-Brown was appointed as a delegate to represent this Society.

The University of Cambridge (England) invited this Society to appoint delegates to assist in the celebrations to commemorate James Clerk Maxwell, and Professor

Kerr Grant and Dr. W. H. Love, B.Sc., were appointed to represent the Royal Societies of each State.

In August, 1931, Dr. William Wheeler, together with other scientists from the Harvard University, arrived in Sydney on a scientific expedition. These visitors were tendered a cordial welcome by the members of this Society.

This year the Clarke Memorial Medal, the most important gift at the disposal of this Society, has been awarded to Frederick Chapman, A.L.S., F.G.S., and on behalf of the members of this Society I offer him sincere congratulations.

Preparations are now well in hand for the meeting of the Australian and New Zealand Association for the Advancement of Science, to be held in Sydney in August next. As this is the third occasion upon which it will be held in Sydney, it is hoped that members will do all in their power to make it a success.

Sectional meetings of Geology, Industry and Physical Science have been held regularly during the year, and excursions of interest were arranged. The best thanks of the council and members are extended to Messrs. H. G. Raggatt, H. B. Bettley-Cooke and G. H. Briggs, Honorary Secretaries of the respective sections, for the lively interest and activities displayed in connection with this important phase of our work.

Details in connection with Science House have already been given by my predecessor, so that it only remains for me to report that the official opening was performed on Thursday, 7th May, 1931, by His Excellency Sir Philip Game, G.B.E., K.C.B., D.S.O., Governor of New South Wales. To celebrate the occasion, exhibits of scientific

and technical interest were arranged for public inspection and lecturettes were delivered as follows:

"The Balance of Life in the Sea", by W. J. Dakin, D.Sc.

"Polar Exploration", by Instructor Commander Moyes, B.Sc., R.A.N.

"What of the City?", by B. J. Waterhouse, Esq., F.R.I.B.A.

"Prospecting by Magnetic Methods", by Major Edgar H. Booth, M.C., B.Sc.

OBITUARY.

It is with sincere regret that I have to report the loss of five members by death, *viz.*:

Robert Grant, F.C.S., elected a member of this Society in 1922, died at his residence, Woollahra, 30th August, 1931, at the age of 66 years. Mr. Grant arrived in this State about 40 years ago and, after spending some time as an Assistant in the Physiological Department of the Medical School at the Sydney University, entered the Health Department and occupied the position of Assistant Microbiologist for many years until his retirement. He took a great interest in his work, and also took an active part in connection with the Chemical Society at the Sydney Technical College.

David Reid, elected a member of this Society in 1914, died at his residence at "Homesdale", Pymble, in his 82nd year. Mr. Reid was born at Peterhead, Scotland, in 1849, and as a youth entered the service of the Nelson Dock Company. He came to Australia in 1871, and joined the firm of Joseph Spilling & Company, Adelaide. In 1877 he was appointed Assistant Manager and afterwards

occupied the position of General Manager for the Orient Steam Navigation Company in Australia until his retirement in December, 1919.

Sydney Hurnett Stroud, elected a member of this Society in 1919, died at his residence at "Dalveen", Chalmers Road, Strathfield, 21st August, 1931, at the age of 41 years. Mr. Stroud was an Englishman who had a brilliant academic career. He was trained at the Bloomsbury Square Pharmacy School, at King's College, London, and was awarded the Pereira Medal—the highest honour for British pharmacy students. He came to Australia in 1914 to a position as Analyst for the Queensland Government, but subsequently joined Faulding's in Adelaide. In 1918 he founded the Pharmacy School at the University of Sydney, where he was Lecturer for several years. He was founder and first President of the University Pharmaceutical Association. He joined Elliott's and Australian Drug Company, Ltd., six years and a half ago, and occupied the position as Laboratory Manager.

William Mogford Hamlet, elected a member of this Society in 1887, died at his residence, "Glendowan", Glenbrook, 18th November, 1931, at the age of 81 years. Mr. Hamlet was born at Portsmouth (England). He was educated at a private school, Bristol. Although a commercial course was mapped out for him and he was apprenticed to a shipping firm in Bristol, he attended the Bristol Trade and Mining School, where he obtained high honours in Science and received the Queen's Medal for Inorganic Chemistry. Afterwards he gained a scholarship which enabled him to proceed to the Royal College of Chemistry, where he studied under Valentine and Sir Edward Frankland. After an appointment as Demonstrator of Chemistry at the Bristol Medical School, he

entered into a contract with the Bristol Agents of the Peruvian Government to analyse the consignments of natural Peruvian guano, then imported from the Chinchas and Guanape Islands. He next received an appointment as Official Public Analyst for King's Lynn. Later he proceeded to the West Indies as Chemist and Assayer for a gold-mining company. In less than two years he was obliged to return to England owing to illness. He was advised to proceed to Australia for health reasons, and came to Sydney in 1883. He was appointed Government Analyst of New South Wales in 1887, and occupied that position nearly 30 years, retiring in 1915. Mr. Hamlet took an active part in the work of the Royal Society and was a member of the Council during the years 1891 to 1897 and 1912-14. He was Hon. Secretary during the year 1898, President during the years 1899 and 1908, and Vice-President during 1900-7 and 1909-11. He also contributed eight papers which are published in the Journal of this Society.

James R. M. Robertson, M.D., Ch.M., elected a member of this Society in 1924, died at his residence, "Vanduara", Elamang Avenue, Kirribilli, 11th April, 1932, at the age of 88 years. Dr. Robertson was a native of Renfrew, Scotland. He graduated at the University of Glasgow. After completing his medical studies, Dr. Robertson passed into the Army Medical Staff. He eventually became Regimental Surgeon of the Black Watch, which he accompanied to India, thence to Burma, where he participated in the Burmese War. Retiring from the Service more than 50 years ago, Dr. Robertson came to Australia, where he qualified as a mining engineer and became well known in the coal trade, especially on the South Coast. For many years he was Managing Director

of the Mount Kembla Coal and Oil Company, Ltd., and until recently took a keen interest in its affairs. Dr. Robertson rendered notable rescue services at the time of the Bulli and Mount Kembla mining disasters. He was the donor of a House to the Burnside Homes, and was a Vice-President of the Highland Society of New South Wales.

John Leo Watkins, B.A. (Cantab.), M.A., elected a member of this Society in 1876, died 1st May, 1932, at the age of 82 years. Mr. Watkins for many years occupied the position of Parliamentary Draughtsman.

Part II.

A REVIEW OF "SYSTEMATOLOGY IN BOTANY".

The systematic classification of plants, or "Systematology in Botany", takes in the study of the whole of the vegetable kingdom. It will therefore be seen that the science of botany plays a most important part in the economic and commercial rôle of any country.

In former years, the study of botany was regarded rather as an elegant accomplishment than as a serious occupation. More recently, however, the subject has changed very markedly because of the wider interests involved, owing to the demand for the closest possible taxonomic classification, in order to serve those in horticultural, agricultural, pastoral and forestry pursuits, and also because of the immense value of the chemical constituents and other commercial products contained in all kinds of plants. Whether we regard the subject from the purely commercial point of view or from the biological aspect, we are bound to admit that to be able to identify any plant with the aid of a description

published in botanical works, even with the aid of the original and possibly typical or authentic specimens, requires high qualities of exactitude, patience and sound judgment.

To institute by comparison, even into minute details, the precise name of any species, whatever its position in the botanical system may be, requires patience and skill and close application to biological studies in plant-life.

Sir Thistleton Dyer, who occupied the position of Director of the Royal Botanic Gardens, Kew (England), in a very lengthy address (1888) pointed out that Darwin devoted many years to the systematic study of plants and animals. It was owing to this fact that he made the following remarks: "No one has a right to examine the question of 'Species' who has not minutely described many." Huxley has also pointed out that: "The acquirement of an intimate and practical knowledge of species making . . . . was of no less importance to the author of the 'Origin of Species' than was the bearing of Cirripede work upon the principles of a natural classification."

A first principle of systematic botany is that a name should denote a definite and ascertainable species of plant. It not infrequently happens, however, that in physiological and ecological literature one will find that the importance of this fact is overlooked. Names are employed which are either not to be found in the books or they are altogether misapplied! It was probably owing to this phase of the subject that Professor Lothar Meyer found himself obliged to defend the position of descriptive science when he remarked that "the physiology of plants and animals requires systematic

botany and zoology, together with the anatomy of the two kingdoms; each speculative science requires a rich and well-ordered material, if it is not to lose itself in empty fantasies".

There is a tendency on the part of certain distinguished personages to endeavour to belittle the taxonomic or systematic division of botanical research, or, in other words, to regard this division of work as being subordinate to other divisions, such as anatomical or histological and cytological researches. Every taxonomic worker should have training in at least two methods of establishing facts, by experiment and by repeated observation. Most facts in physical science are established by experiment, whilst most in descriptive biology are established by repeated observation. In practice, a taxonomist is called upon to classify individuals into species and species into genera. It has been suggested by modern workers that all living organisms of family groups are probably genetically connected. Their lines of descent may not be known to us, but we are able to discover a certain section of the present-day plants connected by a series of intermediate forms or subspecies, which enables us to form some idea as to their origin.

Historical.

The cellular structure of plants was known and described in the seventeenth century, for we are told that the term "cell" was used in a botanical connection by the microscopist, Robert Hook. Writing in 1665, he says, "Our microscope informs us that the substance of cork is altogether filled by air and that that air is perfectly enclosed in little boxes or cells, distinct from

one another." It will be noted that this great discovery was couched in simple terms, characteristic of eminent men of those days.

Some thirteen years later, Nehemiah Grew (1682), an English physiologist, wrote his "Vegetable Anatomy", in which the sexes of plants were mentioned. Then we have Sebastian Vaillant, who wrote a discourse on the structure of flowers, confirming the discoveries of Grew concerning the sexes of plants, while Millington discovered the functions of stamens and thus completed the theory of the flower. Just about this time, Tournefort (1683) published the results of his labours in which a classification was formed, and although generally regarded beautiful in itself, was suited to a very limited number of plants. John Ray was the contemporary of Tournefort, and invented a system of classification even more perfect than that of Tournefort.

Although these eminent men of science did much excellent pioneering work in the realms of systematic research work in nature, the science of botany was of difficult attainment and many new plants could not be reduced to the systems of either Tournefort or Ray. Ray was born in 1628 and Tournefort in 1656, and the latter passed away in 1707, when, in the same year, Linnaeus was born and, as is well known, did remarkable work in the field of natural history during his lifetime. It is chiefly owing to the labours of Linnaeus that the binomial system of nomenclature was established, and that truth, order and precision were introduced into systematicity and cleared away many obscurities in botanical research and formed it into a science. His labours were original, as is shown in the main principles of his classification

of plants and animals into classes. The celebrated classification of Linnaeus was avowedly purely artificial. It was a temporary expedient, the provisional character of which no one realised more thoroughly than himself. This system formed the basis of a classification which was convenient and popular, though not strictly scientific. The terms used by Linnaeus were expressive, as, for example, in Class I (Monandria) all forms of plants with a single stamen were included, and in Class II (Diandra) those plants with two stamens were grouped together, and so on.

It must always be remembered that all plants were originally in a state of nature, hence they are more popularly known as "wild plants". Wild species from which the cultivated forms have been derived are comparatively rare, and very little is known concerning them. Usually it is not possible to indicate a certain wild species as the origin of a particular cultivated race of crop plants. It has been suggested by some writer that in some cases our crop plants are descendants of a mixture of two, three or more species of wild parents; hence these are called polyspecific hybrids. It is probably owing to this that Linnaeus in his "Species Plantarum" reserved pronouncement on the species of *Rosa* and *Salix*. He also suspected that the varieties of *Tulipa, Brassica, Lactuca, Pyrus, etc.*, originated by crosses (Fundamentum fructificat, 1762, p. 21). Part of the last-named varieties, *e.g.*, especially the cultivated kinds of cabbage (*Brassica*), Linnaeus compares with the strains of the dog. Like the parents, the descendants produce continually varying forms. Linnaeus did not acknowledge these as species.

The Inter-Relation of Systematic Botany and Horticulture.

Infinite endless variety is the most striking fact about the plants we cultivate in our gardens, orchards and agricultural areas. Each year catalogues are issued by nurserymen and seedsmen bringing out new (or supposed new) forms or varieties of crop plants for the field or garden. There is a wide variation in cultivated plants. The variations are largely in stature, size and colour of the plants, their foliage and floral characters, as well as in the size, shape and flavour of the fruits.

Systematic botanists appear to have a fear of such plants on the assumption that they are so endlessly variable and so extensively hybridised that ordinary tenets of botanical diagnosis do not hold amongst them. It is probably owing to the latter reason that systematists have, to some extent, neglected the study of horticultural groups and also for the reason that they are not wild plants. Although there is admittedly a wide variation in cultivated plants, there is usually no greater or more inexplicable variation than one meets in any number of wild subjects, with the exception of those termed "archeophytes". The archeological study of plant life is of intense interest, especially in connection with such plants as wheat, rye, cabbage and many kinds of fruit crops, such as apple, pear, plum, *etc.*

The new and more fundamental study of the origin of domesticated plants and of the physiological nature of their plasticities, is now one of the most important fields of botanical adventure because of the vast reams of literature. The plant-breeders' art is but a revelation of the plasticity of the flower in the hands of hybridists and of its environment, and affords us some idea of the forms the flowers of the ages ahead will take. The varia-

tion, such as colour and so-called doubling of flowers, as well as the usual critical characters on which the botanist depends for diagnosis of the species, is occasionally seen in nature, but in cultivated plants these characters commonly remain intact. One soon learns, however, what allowance to make for variation due to cultivation, as one also comes to assess the modifications associated with latitude, altitude, soil, habitat, *etc.*, in wild plants; in fact, the variations are generally less puzzling in wild variables because one is aware of the circumstances behind them. The organic world, as a whole, is a perpetual stream of changing types. Some characters we ascribe to heredity, others to environment, but in many cases neither environment nor heredity seems to explain the appearance of strange characters. Intra-varietal variation is common among many cultivated races of flowers, fruits and vegetables, as will be seen by an examination of the "Everlasting" (*Helichrysum bracteatum*), which is still to be found in its wild state in the coastal districts of New South Wales and other parts of Australia, with yellow or orange-coloured bracts, whereas in the cultivated races there are various shades of colour from white through pale creamy-white, pink, red, purple and orange-red tints.

When the vast range of forms, size and flavour to be found among the cultivated races of apples, plums, peaches, navel-oranges, as well as french beans and other pulse-crops, is considered, it seems difficult to suppose that all this variation is hidden in the original wild form or species. Even in the case of hybrid groups produced by artificial means, one is usually surprised, on careful study, to find how readily the parental traits and botanical characters still remain and can be traced to their

ancestors. In the plant world, as in human beings, exact likenesses, as seen by the eye of the specialist, are rare, and this is true, even when plants are of the same variety, coming from the seed produced by many generations of inbreeding. What is still more striking, however, is the diversity of varieties among plants propagated by cuttings, budding and grafting, or by offsets or shoots of plants which are only isolated parts of the same plant, *e.g.*, the sporting silver-chain geranium, carnation, and the navel-orange.

Mendelian and other studies have taught us to look for somewhat predictable breakups in the seed produce of hybrids, yet the supposed crosses are habitually propagated by seeds and may not show dominants and recessives, and the question then arises whether the group is, in fact, of hybrid origin. One, of course, must be careful not to accept the "hybrids" of the horticultural trades too confidently. Many of the plants cultivated in nurseries and gardens have been named and recorded in catalogues by persons with very slight (if any) technical knowledge of the floral or foliar characters of the plants so-named, and who in numerous instances, through ignorance, have adopted the practice of giving binomials to minor forms and varieties, a custom which would be largely avoided if adequate instruction in the elements of systematic botany were provided in horticultural organisations. One of the main causes of this trouble is the fact that we have no consistent and adequate records of horticultural plants when contrasted with the methods of describing and recording the indigenous flora. Catalogues are unsuitable for records of new forms or varieties of horticultural plants; neither are lists of names published in newspapers or other publications of

this nature reliable, because of the omission of proper descriptions in most instances and, where descriptions are given, as in catalogues, there are no opportunities given to check them for comparison with those already described by properly constituted societies, where members are interested and are afforded opportunities of inspection and discussion as to the merits of such proposed new forms. Cultivated plants should be studied from a botanical point of view just as closely as plants found in a state of nature, and should not be left to the untrained cultivator.

It has been stated that there is some difficulty in identifying plants by the use of scientific treatises, and that an endeavour should be made to substitute a system based on the use of more easily observed characters. This phase of the subject, as I have already shown in an address to the Linnean Society of N.S.W. (1931), is extremely difficult, because of the hopeless confusion connected with colloquial or vernacular names applied to our Australian plants, and which are often quite distinct from those used in connection with the same plants in other countries where they are cultivated extensively. The same difficulties would obtain in connection with plants of other countries owing to the lack of authoritative registration, mechanism and other co-operative action among horticulturalists and because of the disappearance of scores of thousands of horticultural varieties which have not been preserved in herbaria or by drawings, as is the case with plants collected in a wild state. The confusion in common names has been, of course, even worse than in scientific names, because of the reasons stated above. A single plant may have hundreds of names, some very closely localised and some

very wide spread. For example, Van Wijk's Dictionary of Plant Names credits the European Water Lily (*Nymphaea alba*), with 15 English, 44 French, 105 German and 8 Dutch names—a total of 245 vernacular appellations. A well-arranged standardised list of the vernacular names, with the corresponding scientific names, would prove highly useful. Native or popular names are only a means to an end—not the end of inquiry itself. Although frequently misapplied, they are useful, as they act as a key to further enquiries.

There should be no difficulty in obtaining the acceptance of scientific nomenclature in commercial circles, as it offers a larger measure of security for the authenticity of the plant product than the popular name. To the nurseryman or seedsman who is confronted with the danger of legal proceedings being taken for supplying an article not true to name, this consideration would make a special appeal. We are compelling the farmer and pastoralist, under statute authority, to learn both a common and a botanical name for his weeds, the former a concession to popularity and the latter as a legal safeguard, and the duplication and multiplication of their vernacular names promise, in the near future, to impose a heavy burden on municipal and shire clerks and inspectors charged with the administration of the Noxious Weeds Act. Officers of the Forestry Departments, as well as those connected with the Stock Branch and Education Department, are frequently puzzled by the disparities in popular nomenclature obtaining in their respective spheres of plant studies. To the scientist investigating the properties of plants, especially those dealing with the timber resources, the stability of the botanical name makes a powerful appeal.

The following extract from the Report of the Executive Committee of the Commonwealth Advisory Council of Science and Industry (July, 1917, p. 34) is pertinent to this phase of the subject: "It must not be forgotten that chemical researches in vegetable products are practically valueless unless the plant from which the product was obtained has been scientifically classified so as to be identified by its botanical name. A good deal of the work carried out in Australia in the past has been wasted, owing to the uncertainty as to the exact source of the material employed. Hence, in this type of work, systematic botany must precede chemical research."

In advocating the use of botanical names by which the plants are already known throughout the world to those trained in taxonomical work, attention might be drawn to the fact that botanical names are identical with a language which acknowledges neither racial nor geographical boundaries. The nomenclature is therefore based chiefly in Latin terms, so that the whole community of every country shall have a fairly definite basis to work upon when working out the various groups of plants which biologists call species.

Illustrations of Flowering Plants, Ferns and Fern Allies.

Sixty-four years ago, in 1855, George August Pritzel, Archinarius and Librarian of the Prussian Academy of Sciences in Berlin, published his first edition of the Iconum Botanicarum Index, and in 1866 he issued a supplementary list of references up to the end of the year 1865. These two volumes, which contain over 107,000 references to illustrations of flowering plants and ferns, have remained until now the standard alphabetical

register or book of references to the illustrations of plants which have appeared in botanical, horticultural and other publications. In 1917 the Council of the Royal Horticultural Society of London, on the advice of their Scientific and Horticultural Committees, decided to undertake the revision and continuation of Pritzel's Index, under the title "Index Londinensis". The new edition, compiled from botanical and horticultural publications of the eighteenth and nineteenth centuries, has been prepared under the auspices of the Royal Horticultural Society of London at the Royal Botanic Gardens (Kew), England, by Dr. Otto Stapf, and includes the references in the original Index, with the addition of nearly 500,000 references to illustrations of flowering plants, ferns and fern allies published in botanical, horticultural and other works and journals between the years 1753 and 1920 (inclusive). This is a most valuable compilation, which will be much appreciated by botanists all over the world.

Jordan's Law.

The term "Jordan's Law" or the "Law of Geminate Species" was originally applied by Dr. Joel A. Allen (who accepted the generalisation propounded by Dr. D. S. Jordan) to Jordan's theory, which may be briefly stated thus: "Given any species in any region, the nearest related species is not likely to be found in the same region, but in a neighbouring district separated from the first by a barrier of some sort or, at least, by a belt of country the breadth of which gives the effect of a barrier." In a subsequent work, Jordan stated that the adoption of this term "rests on the observations of many workers, for it is a matter of common knowledge among

field naturalists that the minor differences are due to some form of isolation with segregation".

Selection produces adaptation. By some barrier or other, the members of one group of plants are prevented from interbreeding with those of another group. As a result, local peculiarities are fixed. "Migration holds species true, localisation lets them slip" or rather leaves them in the backwash of currents of evolution. Peculiarities thus set off by isolation become intensified by in-and-in-breeding or segregation, and the particular environment exercises some continuous type of selection until at last there emerges a new form recognisable as distinct.

It has been suggested that geminate species are merely forms and not species in the true sense of the term. Jordan regards this assumption as merely hypothetical, as interbreeding is no test of species.

In his studies of the species *Draba verna* of Linnaeus (*Erophila draba* of modern authors), Jordan (1873) distinguished no less than 200 forms, each of which is stated to have prescribed to its own special characters for many generations with complete constancy. Horticulturalists have found exactly the same thing to happen in roses, pansies and other forms of plants of floricultural interest. Fruitgrowers have raised numerous forms of fruit. Market-gardeners have catalogued thousands of forms of wheat, oats, barley, and other crop plants! Some of these, we know, do not breed true, just as Sarton (1905) has found that in some so-called Jordanian species some are good species and some are not. Some so-called Linnaean species we find share the same fate, and so we shall find in all classes of plant life the individuals

of a crop interbreed freely. Therefore, a species is a mixture of genotypes or biotypes, freely interbreeding and containing some types of homozygotes as well as several type of heterozygotes or hybrids. It is interesting to note that Shull (1906), after a review of Kupffer's paper on Kolreuter's methods of distinguishing species, based upon the sterility of hybrids, especially among the Violaceae, concludes that when a supposed hybrid shows much less fertility of the pollen than its supposed parents, it is not a necessary but a sufficient proof (1) that the supposed hybrid is truly hybrid, and (2) that its parents belong to distinct species. Just how far a study of the pollen of various forms will aid in the classification is a matter of much further research than at present obtains. Swingle (1928) on "Metaxenia in the Date Palm" and Nixon (1928) on "The Direct Effect of Pollen on the Fruit of the Date Palm" and the "Immediate Influence of Pollen", have shown that there is a vast field of research to be opened up which may reveal wonderful results. For example, it has been discovered that the pollen of "Canary Island Palm" (*Phoenix canariensis*) used on the "Date Palm" (*Phoenix dactylifera*) produces a small peculiarly pointed seed, quite different from the ordinary date seed, and small or medium-sized fruit that ripen late. On the other hand, pollen from the tiny palm (*Phoenix roebelinii*), which has the smallest fruit seeds of any wild form of Phoenix known, when used to pollinate the true date palm, causes the formation of large seeds, usually with a curious sunken area about the germ pore, and makes large dates which ripen extremely late—nearly two months later than the ordinary crop. Preliminary tests of *Phoenix sylvestris* from India seem to give medium-sized dates, ripening earlier.

The economic importance and scientific interest of these discoveries, if followed up, may lead us to a greater understanding in connection with the chemistry or rather the physico-chemical system of plants.

We know that chemical substances are affected by the reaction of mineral substances contained in the soil. We see marked changes in certain plants when grown in different soils or when manures are incorporated in liberal quantities, but we know very little concerning the taxonomic physiological problems, especially the inter-action caused by enzymes in the marvellously delicate co-ordination and regulation of the vital processes by which the life of the organism is maintained.

Climatic and soil conditions may alter the facies of a good strain of crop plants, yet it may be noted that even under the best climatic and soil conditions a bad strain can never be made to produce a good flavoured fruit. It is only through the introduction of new elements conveyed by the aid of pollen grains that good qualities or improved yields, *etc.*, can be effected. As an example of this, I may mention that in my investigation in connection with the breeding of sugar-cane seedlings at the Colonial Sugar Refining Company's nurseries at Lautoka in Fiji, I found that for a number of years seedlings had been raised from the variety "Badilla" without any improvements being made in the sugar content. When critically examined, it was found that although there were a number of arrowing canes produced by this variety, and a certain quantity of fertile seeds collected, the anthers had no perfect pollen grains present. There were, however, two other varieties, namely, "Clarke's Seedling" and "Varus", which produced an abundance of fertile pollen grains. As these two varieties were

usually grown in close proximity to the variety "Badilla", there could be no doubt that the latter variety was pollinated with pollen from these two varieties. When I questioned the plant-breeder (Mr. W. A. Speight) concerning the quality of "Clarke's Seedling" and "Varus", he frankly admitted that both these varieties were much inferior to the variety "Badilla" so far as the yield of sugar content was concerned. In view of this, we can only arrive at the conclusion that as there were no fertile pollen grains present in the florets of the variety "Badilla", this variety was pollinated with pollen from inferior sugar-producing forms, and thus the offspring or resultant seedlings could not be expected to give improved yields.

Soil and Chemical Factors in Connection with our Conception of Species.

There is at times some difficulty in differentiating between two or more forms of the same species, which, though distinct physiologically, cannot be separated on any structural characters. Several such physiological strains or races or forms are known to exist in Australian species of the genera *Eucalyptus, Leptospermum* and *Geijera*.

It is known, for example, that there are three distinct physiological forms of *Leptospermum Liversidgei*, and at least three (or maybe four) of *Leptospermum flavescens*. Two of the latter grow side by side in the neighbourhood of Hilltop on the Main Southern Line. One of these forms has branches or young twigs with a distinct purplish-red colour and even the leaves are seen to be of a dark colour owing to the anthocyanin pigment present in the leaves as well as in the young twigs. Mr. A. R. Penfold, in his

chemical researches (1922) has shown that there are at least two distinct forms, and possibly three distinctive forms of essential oils in the species *Leptospermum Liversidgei,* and a similar condition of affairs is also recorded for *Eucalyptus piperita* by Penfold and Morrison (1924), and for *Eucalyptus dives* by the same authors (1927, p. 54; 1928, p. 72; and 1927, p. 79).

We have also received reports that there are two forms of the well-known "Wilga" (*Geijera parviflora*), one of which is eaten ravenously by sheep, whilst the other, growing side by side, is not touched.

The question naturally arises: What is the cause of these changes of colour factor or chemical substances in plants apparently belonging to the same species? In connection with cultivated plants it has been suggested that the effect of cultivation, *i.e.,* good living and good feeding, has in some way broken down the constitution of the plant and that this has given rise to a tendency to vary. This suggestion may be all very well when applied strictly to cultivated plants, but as yet we have no definite evidence in support of this view. We know that certain plants, such as Rhododendrons and some forms of Azalea, thrive in peat and sand mixture because the chemical reaction of the soil is acid, and that they die in the ordinary fertile garden soil because the reaction is neutral or alkaline. Experiments conducted by F. V. Colville (1927) have shown that aluminium sulphate applied to equal parts of loam, manure and sand which was neutral or slightly alkaline in reaction, gave a definite and pronounced stimulation of growth. The aluminium sulphate treatment has also been applied to "Blueberry" or "'Cranberry" (*Vaccinium* spp.) and *Gordonia* (*G. pubescens,* syn. *Franklinia alatamaka*) in

an unsuitable soil with the same stimulating results obtained in the experiments with Rhododendron (*R. catawbiense*).

Certain varieties and species of plants when exposed to new sets of conditions, develop new traits and characters, as, for example, the so-called "Prickly Pear" (*Opuntia inermis*) of America (which has become a serious pest in Australia) and the "Mexican Rubber" or "Guayule Rubber" plant (*Parthenium guayule*). The latter failed to produce as much rubber when taken away from its desert environment and cultivated, whilst the former was never regarded as a pest plant in its native country, but has spread at an alarming rate in Australia.

Consideration of the chemical substances in plants commenced at an early date; in fact, we may consider this as the real starting point in the study and researches in connection with plant life, yet in reality we know next to nothing concerning the physics and chemistry of plant life as an aid to taxonomic work. Bateson (1914, p. 9), however, has stated that "the characters of living plants are bound up in properties of colloids and are largely determined by the chemical powers of enzymes, but the study of these classes of matter has only just begun". It may be that a closer study of biochemistry will reveal certain endomorphic characters which will explain the complex nature of the chemical changes in the living plant.

We are told by Blackman (1908) "that enzymes are of biological origin and are of great importance in the various activities of living matter, and that life is just one enzyme reaction after another. Enzymes are formed by all living cells. Whether these carry on all the functions of an organism, as in the case of unicellular forms

of life, or are devoted only to specialised functions, as in the higher plants, is a matter for further investigation.

"The only difference between these two types of cells is that in the former all the enzymes are produced in a complex mixture, whilst in the latter they are usually specialised and are readily separated, since different types of cells may produce certain enzymes in greater concentration than do other cells in the same organism. It will thus be seen that biological processes may be differentiated into those performed by enzymes and those of living protoplasm. The enzymes enable the cell to carry on the various hydrolytic and synthetic processes. Within the cell they transform organic and inorganic substances for the production of energy and also play a part in various intra-cellular syntheses. Of the metallic elements which are essential for the growth of plants, some occur in such minute quantities that one can only imagine their function is catalytic. If iron, for instance, played any part in metabolism which involved its being used up in any building material or by-product of metabolism, then a larger amount than suffices should be advantageous. If its function is catalytic, the iron would go on acting indefinitely without being consumed, and so a minute trace might serve to carry out some essential and even considerable subsection of metabolism. Elements like magnesium, manganese and iron are often associated with non-vital catalytic action.

"Metabolism is essentially a catalytic process. In support of this we know that many of the inherent parts of the protoplasmic complex are catalytic enzymes, for these can be separated out of the protoplasm, often simply by high mechanical pressure.

"If metabolism is a complex of up-grade and down-grade changes catalysed by protoplasm, we must expect the amount of metabolism to obey the law of mass, and to be proportionate to the masses of substances entering into the reaction."

The question of making a species an indefinite entity and then giving varietal name to what may be considered the typical form on the one hand and, on the other, fixing for all time a malformed or freakish specimen as the type, is a practice that should be strenuously opposed by systematists.

Two examples of this method of determination may be quoted in connection with very common Port Jackson plants, namely, *Acacia decurrens* and *Callistemon lanceolatus*. The latter was originally described under the name *Metrosideros citrina*. When the genus *Metrosideros* was split up into smaller genera, the species *M. citrina* of Curtis (1794) was placed in the genus *Callistemon* by De Candolle (1828) under the name *Callistemon lanceolatus*. According to modern methods of classification, it is agreed that the earlier specific name must be taken up; the species therefore should be *Callistemon citrinus*. Dr. Otto Stapf (1924) has correctly made the new combination, but in making the transfer has created a new name, *Callistemon citrinus* var. *splendens*, for what we know as the typical form of plant commonly known as "Scarlet Bottle-brush" along the coastal districts of New South Wales. There can be no doubt that the plant originally described as *Metrosideros citrina* was raised from seeds collected from plants of the common Scarlet Bottle-brush. As it was grown in a greenhouse in England under artificial conditions, the plant was unable to produce perfect flower-

ing spikes as we see under natural conditions in Australia. The flowering spike figured by W. Curtis in 1794, although representing the type of the species, is not characteristic of the species as we know it, and therefore should not be regarded rigidly as the standard for comparison for all the population of the species. We should make due allowance for such freak or malformed material which occurs in many populations of the different species of this and other genera, particularly when we know they are grown in unnatural conditions. I have collected specimens from at least three different species of *Callistemon*, showing the flower in the axils of the leaves instead of forming a spike in the true sense of the term. I have also collected specimens of different species of the genus *Callistemon* having five or seven longitudinal nerves instead of the usual central mid-vein and intramargin nerves characteristic of the genus. Whilst this kind of deviation from the normal form of growth may be of special interest to teratological specialists, they should not be regarded as other than malformations or freakish growth by the systematist. When it has been discovered that through inexperience or perhaps ignorance, a species has been described which does not show the normal characters of a population of plants, it should be the duty of the whole school of systematists to rectify such errors instead of taking advantage of such freakish developments as a laudable excuse for establishing specific or varietal names.

In the so-called *Acacia decurrens* series we have a very considerable amount of confusion and indecision, caused through certain botanists having sunk the original species described as *Acacia decurrens* by Willdenow (1802) as *Acacia decurrens* var. *normalis*. What may

be regarded as the typical species described by Willdenow is represented by an extensive population of these plants in a state of nature in the Sydney District, extending to the Blue Mountains of the Western Districts and on the Tablelands of the Southern Districts of New South Wales. It is only found on the better class soils, and is in flower during the spring, August to September. On the other hand, *Acacia mollissima* of Willdenow (1802) is usually found on poorer soils of the Southern Slopes of New South Wales, extending to Victoria and Tasmania, and is usually seen in flower during November and December. The two species are quite distinct and should never have been confused because of the distinctive botanical characters and seasonal difference or flowering periodicity. *Acacia dealbata* and *Acacia irrorata* have also been confused with and described as varieties of *Acacia decurrens,* but are abundantly distinct. A species recently described under the name *Acacia filicifolia* Cheel and Welch (1931), has also been confused with the above, together with *Acacia arundelliana* of Bailey. The latter might easily be regarded as an extreme form of *Acacia irrorata,* Sieber (1826) (syn. *Acacia pauciglandulosa,* F.v.M.), as has been suggested by Maiden (1908), but cannot by any means be regarded as a variety of *Acacia decurrens.* The possession of type specimens in such circumstances as related above does not entirely remove the difficulty in correctly diagnosing specific difference, because of the omission of information in connection with the environmental conditions under which the type existed. The most valuable aid to the taxonomic botanist is personal observation of the plants in situation, but this is frequently impracticable. Many instances could be quoted as to the need for exten-

sive field work for the purpose of studying the factors liable to affect the morphology of leaves, *etc.* This class of work can only be achieved in a satisfactory manner by those who had the necessary training in the work; otherwise the information will be largely speculative.

There are very few research workers at the present time who can provide a body of fact demonstrating the variability of living things in nature. Darwin regarded variability as a property inherent in living things, and with him began a general recognition of variation as a phenomenon widely occurring in nature. On the other hand, we have Hooker's views (1853) as follows: "The result of my observation is that differences of habit, colour, hairiness, and outline of leaves . . . . are generally fallacious as specific marks, being attributable to external causes and easily obliterated under cultivation."

It is probably owing to the close relationship which existed between Bentham and Hooker that we find in the Flora Australiensis so many compound descriptions (or mass morphology) which were drawn up to comprehend what is known as composite species.

Some of the descriptions cover a wide range of so-called forms or varieties, which, by certain botanists, are called subspecies. These are sometimes grouped around a mean type, and are represented as being extremely polymorphous, and the limits between the so-called forms, varieties, subspecies or species are often extremely vague. It is interesting to note, however, that Bentham offers sound advice when he frequently and frankly admits that many of his generalisations may be wrong, and freely advised that such can only be remedied by local botanists.

Prof. N. T. Vavilov (1922) has defined a Linnean species as "a separate morpho-physiological system con-

nected in its genesis with a definite environment and area". He further regards them "as actual complexes, actual systems, which exist in Nature and represent important definite links in the evolutional chain, the knowledge of which is very helpful in mastering the multifariousness of the organised world". The concrete material shows that the so-called "Linnean species" may be very different in regard to their contents. "Being more or less separate systems, they manifest themselves in a different compass. The analysis of a great number of Linnean species by means of the method of differential systematics and differential geography, as well as by the modern methods of genetics and cytology, reveals the great diversity of the species. Thus there are sometimes bulky systems belonging to one Linnean species which might be expediently subdivided into categories or subspecies. Sometimes, on the contrary, a Linnean species represents a very limited and comparatively small system."

No matter what differentia are adopted to separate one species from another, it naturally follows that the visible characters will be the first criteria selected in the field by naturalists and taxonomic botanists when collecting specimens for study.

In horticultural operations a much finer discrimination of morphological characters has been adopted by trained specialists for purposes of classification in cultivated plants. The same remark may be applied to those dealing with agricultural crop plants. We have only to review the trade catalogues of both horticultural and agricultural seed merchants, when it will be seen that scores of thousands of roses, chrysanthemums, dahlias, apples, plums, wheat and potatoes are offered for sale

under distinctive trade names. This very fact alone should convince those authorities in charge of our large institutions, such as the National Herbaria and Botanic Gardens of the various States of the Commonwealth of Australia, of the need for closer attention to details, and for a broader outlook on the most difficult tasks imposed on the limited number of workers in this particular phase of botanical research.

In some instances the species are not so sharply defined as the descriptions in the floras would lead one to infer. An example of this may be cited in connection with *Eucalyptus pimpiniana* and *E. Isingiana.* The latter, although described as a distinct species, was found to be, when critically examined, the more matured stage of development of the former, and, strange to relate, the collector of the specimen of *E. Isingiana,* when forwarding additional specimens collected from the same tree which formed the type of *E. Isingiana* was informed that they could not be separated from *E. pimpiniana,* although previously informed that it was a new species.

Instances of this kind frequently occur owing to the fact that the systematist does not have the opportunity of examining the live plants in the field. On the other hand, there are plants which are so strikingly similar as regards certain characters that we are able to group them together into families, genera and species. Certain characters appear to be less variable than others, both inherently and when subjected to difference in environment, and these are then regarded as fundamental characters and are often made the basis for the groupings mentioned above. This grouping or classification, however, is in many respects artificial, and must always

remain more or less so, serving largely as a convenient method of cataloguing or keeping track of them.

Every plant has two names, a generic and a specific one. The generic name indicates the group to which the plant belongs, and the specific refers to its own individual characters. Amongst the flowering plants, our present knowledge of systemity is sufficiently definite as regards genera for there to be little confusion possible in that connection. However, in the case of specific names it is otherwise, and it is quite common to find the same plant called by different names by different botanists. For this reason systematology is a very important branch of botanical research and until systematic biologists are able to arrive at some solution as to what really constitutes a specific difference, we shall never be able to establish a stable system of nomenclature which is so essential for trade purposes as well as for research work.

In general, there are two classes of systematists familiarly known as lumpers and splitters. Either extreme, of course, is wrong, but in the light of modern biology the tendency to excessive subdivision is perhaps the worst. The point to be observed is that so-called species is not a fixed entity. Species are constantly changing by slight mutation, or by acquired variation, that is to say, there are no identical individuals in nature, but similar ones only, and this fact alone suffices to make the species conception an uncertain one. Absolute and permanent fixity of botanical nomenclature in such cases therefore cannot be ensured. There will always be certain biological peculiarities as well as physiological differences in plant life. These differences are inevitable and are independent of rules and arbitrary decisions, chiefly through lack of complete knowledge. New facts as to

structure and other considerations are constantly being brought under notice and must be adjusted.

In modern genetical literature, species and their subordinate units are often spoken of as populations which, according to Du Rietz (1930), is synonymous with Plate's "Individuengruppen" and regarded as a very sound and stimulating method of treatment. Du Rietz also applies the term population-concept to all sorts of taxonomical and plant sociological units and treats them as concrete populations, and regards the problem of the definite or arbitrary nature of the border-lines between the populations accepted as units as of far more importance than the purely theoretical discussions, and states that the genealogical continuity of the species must not be forgotten.

In his treatment of the "individual" Du Rietz (1930) states: "The most elementary unit of taxonomy is the individual. The limits of an individual are not always easy to define, but most biologists of the present day agree that the soundest definition is the physiological one, *i.e.,* that the main criterion of an individual should be its physiological autonomy. Thus, in cases of vegetative propagation, a new individual is formed with the break of the connection with the mother-plant."

Du Rietz admits that theoretical and practical complications may arise in several cases, especially in the case of vegetative segregation and in colonies of closely connected individuals. The vegetative segregations and colonies of individuals are defined by Du Rietz (1930) as follows:

The Clone: "A clone is a population consisting of the vegetative (asexual) descendants of one individual."

The Pure Line: "A pure line is a population consisting of the individuals formed by strictly autogamous reproduction of one homozygotic individual."

The Biotype: "A biotype is a population consisting of individuals with identical genotypical constitution."

The Form: "A form is a population of one or several biotypes occurring sporadically in a species-population (not forming distinct regional or local facies of it) and differing from the other biotypes of this species-population in one or other several distinct characters."

The arrangement of groups may be made in the following manner:

REGNUM VEGETABILE.

Cryptogams	Phanerogams.
Gymnosperms	(Angiosperms.)

Division
Subdivision
Class
Sub-class
Cohort
Sub-cohort
Family
Sub-family
Tribe
Sub-tribe
Genus
Sub-genus
Section (Hairy, Glab.)
Sub-section
Species
Sub species (Vel proles, gall Rae)
Varieties
Sub-varieties
Variatio
Sub-variatio
Planta.

"Index Kewensis", an enumeration of the genera and species of flowering plants from the time of Linnaeus to the year 1885, was compiled at the expense of Charles R. Darwin, under the direction of Sir J. D. Hooker, by B. D. Jackson (1895). Since the publication of the original, seven supplements have appeared (1921-1925), the seventh containing some 33,000 new specific names and new combinations. So far as I can ascertain, no attempt has been made to give an exact account of the number of specific names actually published in this most comprehensive and valuable work, nor of the standard species in contradistinction to those regarded as synonymous. The reason for this is, no doubt, owing to the differences of opinion as to what constitutes a species.

Various estimates have been made as to the number of valid species of plants that have been discovered and described in scientific literature, but so far we do not seem to have any reliable figures because of the differences of opinion as to what actually constitutes a standard species. In 1902 Professor Vines estimated the world's flora at 176,000 species. In 1907 Dr. Alfred Russell Wallace gave the number as 136,000 species, or 40,000 less than Professor Vines. Then we have J. H. Schaffner's estimate of 194,311 species.

If we review the figures given for Australia it will assist in the realisation of the difficult task set for present-day systematists in making a determination of plants sent in for identification. One hundred and sixty-two years ago, Banks and Solander made a collection of about 1,000 species of Australian plants. During the years 1802-1805 Robert Brown brought the total to 4,200 species. Baron Ferdinand von Mueller in his census (1889) brought the number up to 12,049 species com-

prised in 1,617 genera. Since the publication of Mueller's census, about 2,360 additional species have been described, so that we can roughly estimate about 15,000 species for Australia. When we contrast this number of species with that stated to have been recorded for Europe by Robert Brown, *viz.,* 33,000 species, it will be seen that a vast amount of useful botanical research work has been conducted by a very limited number of workers when compared with the older countries with much greater populations. In addition to the angiosperms (flowering plants) and ferns, there are vast numbers of cryptogams recorded in scattered literature which have to be accounted for, and may exceed the numbers quoted for the higher forms or species of plant life.

Mendelism.

The term "Mendelism" in connection with plant breeding problems has been used very freely during recent years because Gregor Mendel was the first to apply the genetic process in certain experiments with peas, *etc.* In these experiments Mendel detected heredity factors. These are now considered by certain botanists to be more natural and consequently more important for classificatory purposes than the floral organs of plants. Since Mendel's important discovery in 1866, however, followed by such eminent authorities as Correns, De Vries and Tschermak in 1900, who conducted work on similar lines, many important modifications of Mendel's original conception have come about. Foremost among these is our conception of what constitutes a character. The vague meaning attached to this term by the older school of biologists is gradually being replaced by the usage of the chemists and physicists. In this sense a character must

always be looked upon as a combined result of heredity and environment. It is considered by some authorities that the heredity units themselves are not characters in any sense of the term, but, in conjunction with environment, express themselves as characters.

The practical experimental study of variation and heredity has opened up an entirely new field of study, and largely accounts for the question as to which group of organisms has a right to be called a species. The question is answered in different ways because of certain discoveries, as, for example, in unisexual plants. Unisexual plants have one set of sex organs—male and female. The male plant may have certain characteristics different from the female, and these are quite independent and are distributed solely or predominantly by one sex. Because of this it has been suggested that we cannot define a species as a group of organisms having the same genotype, for it is known that often the male and female species of one species (as at present understood) differ in the number of their chromosomes and in the number of their genes. It will thus be seen that whilst cytological findings are helpful in one set of circumstances, they are apparently of no value in others. Dr. W. Bateson brought Mendelism into vogue in England, and when delivering his presidential address during the visit of the British Association for the Advancement of Science in Melbourne and Sydney in 1914, very cleverly defined the genetical process as follows: "Two germ cells unite to produce each individual body." He also pointed out that "the individual body is a double structure, whereas the germ cell is single". It will thus be seen that plants are formed as pieces of living material split from the body of the parent organisms.

If we make a closer study of cytology, we shall find that the living cell contains a body which is called the nucleus; this nucleus has a rather complex structure, and it has been observed that when it is going to divide it consists of distinct microscopic elements of distinct shapes called chromosomes, easily seen when using certain dyes for staining. When the cell is going to divide, the chromosomes split longitudinally, and half of each chromosome goes to one of the two new cells to be formed, the other half to the other daughter cell. In this way the plant keeps always the same chromosome number. All the individuals of the same species have this character throughout, except when the plant produces sexual cells—gametes. The gametes contain always only half the number of the other (the so-called somatic) cells of the individual, and fertilisation consists in the fusion of a male and a female gamete, each with the half chromosome number, thus ensuring full numbers again in the fertilised cell, the so-called zygote.

The discovery that every species carries in the nucleus of every cell a definite complement of chromosomes and a peculiar complex of specific genes causing intra-fertility and intra-sterility, is a great advance in our knowledge of the nature of a species. It has also shown that genetic factors are definite things, either present in or absent from any germ cell, so that we may distinguish an individual plant as a pure-bred for any particular factor or its absence.

This new knowledge has been developed by the co-operation of systematists, cytologists and geneticists, and bids fair to revolutionise the modern new Darwinian conceptions of the arbitrary nature of species. Experimental evidence shows that a species is a real entity composed

of characters, chromosomes and genes peculiar to itself. It has been stated by Phillip (1931) that "the study of somatic segregation is important genetically for at least two reasons. One reason is that many horticultural varieties of plants have their origin in that type of somatic segregation which is called bud-mutation. A second reason is that a somatic segregation may or may not be sexually heritable, hence offering no little difficulty to a geneticist who is studying the inheritance in crosses in which one of the parents of the two used arises in bud sports." The examples given in support of this statement are experiments with *Manihot utilissima* and *Hibiscus rosa-sinensis*. It will be gathered from a close study of genetics that a case has been made out for taking the chromosomes to be the important organs of heredity. They are permanent. They generally reproduce themselves exactly at each cell division. They alone are contributed equally, in normal cases, by both parents at fertilisation. They provide a mechanism of reproduction which enables us to understand why the germ cells of a biotype may be pure and contain material derived from only one parent in respect of characters in which the two parents differ. Finally, the chromosomes are different from one another so that if a part of one is doubled or lost, the qualities of the whole are more or less sharply defined. It has also been noted that chromosomes of closely related species may be very different both in number, size and form. There is then in the chromosomes, material for the study of variation in plant life.

Homozygism and Heterozygism.

It was stated by Bateson (1914) that "the only definable unit in classification is the homozygous form

which breeds true". The true breeding forms which Jordan (1873) is said to have distinguished in such multitudes, are considered by some to be real entities. They have been variously termed elementary or micro-species, and are supposed to represent smaller and more sharply defined classificatory units. Many systematists prefer to regard them as species in the making and to pool them into arbitrary Linnean or composite species, for the convenience of collectors and for the simplification of catalogues. It must be admitted that the broad species concept of the older school of systematists has served a very useful purpose. Whether we are ready at the present time to upset the old order of systemity is an open question. We know that the modern trend of scientific investigation seems to indicate that many plants which are at present classed as species by some botanists may be hybrids.

Dr. J. P. Lotsy, who visited New Zealand and Australia during the year 1925, suggested that "each main class of animals and plants originally formed one vast syngameon, originating from an accidental cross of widely differing biotypes of an older syngameon". Du Rietz (1930), in commenting on this, states: "But even if this be true, the reconstruction of the whole process of differentiation of those immense syngameons of decreasing size appears anyhow to be a rather hopeless task. Our division of the main classes of animals and plants into orders, families, genera, *etc.*, must, therefore, to a large extent be carried out in the rather artificial way of grouping the species, genera, *etc.*, simply after their morphological resemblance. The same method must often be used even for the grouping of the species within a genus, at least until the commiscuum and comparia

within that genus have become sufficiently known. The more this purely morphological method can be combined with geographical, paleontological, genetical and cytological methods, the greater is the chance that it will ultimately be possible to reconstruct the old syngameons within the group concerned."

It is known that presumed stable genotypes or elementary (micro) species give rise when crossed to unstable heterozygotes, which segregate into a new series of biotypes. This I have already proved in my own experiments with "Soy Beans" (*Glycine hispida*) and "French Beans" (*Phaseolus vulgaris*). For a number of years I cultivated four varieties of "Soy Bean", *viz.,* yellow, green and two black-seeded forms. One of the latter is known in the trade as "Ebony". When crossed with a green Soy, known in the trade as "Guelph", the resultant seeds or F_1 generation were of a yellowish-green colour. When these seeds were sown the resultant crop or F_2 crop generation gave two-thirds yellowish-green seeds almost identical with the F_1 crop, and the rest were a mixture of seeds, some of a distinctly pea-green colour, others black and others brown. When the F_2 seeds were sown, the yellow-green seeds gave similar results as the F_1 generation, but the pea-green and black seeds bred true, whilst the brown coloured seeds were nondescript brown tending to black. In my French Bean experiments I obtained some seeds known in the trade as "Black Wax". From these I noted a plant producing mottled coloured seeds instead of black, and was unable to match them with any form in my collection of upwards of fifty sorts, or with any other form known in the trade. As I had not made the cross, I arrived at the conclusion that it was a mutant or was probably the result of an

accidental cross by bees or other insects. When the F_1 (mottled seeds) were sown, the resultant crop gave two-thirds mottled, almost identical with the parent form, and the rest were a mixture of white and black seeds. Two successive sowings gave similar results from the mottled seeds, but the white-seeded forms bred true, whilst the black-seeded forms were variable in shape, but of a dullish black colour.

In connection with some experiments in crossing two species of Bottle-brush (*Callistemon*) some interesting results were obtained in the shape and venation of the leaves, as well as in habit of growth. In October, 1909, I pollinated the pistils of *C. acuminatus,* native of Bullahdelah, in the Port Stephens District, with pollen from *C. citrinus* (*C. lanceolatus*) common in the Port Jackson District. The seed capsules containing the minute linear seeds were gathered in 1912 and sown in November, 1912. Only six plants were raised and brought to the flowering stage in October, 1915 (see Cheel, 1917). The foliage characters of the F_1 generation were intermediate between the two parents so far as the shape is concerned, but the venation was prominent like the mother plant (*C. acuminatus*), and the habit of growth was most vigorous in all the seedlings. The flowering spikes were also longer. Seeds were obtained from the hybrids some three years later and sown in November, 1918. Several seedlings were raised and planted out and examined when in flower during 1921. Two plants were noted as having vigorous growth and strongly veined leaves like the mother plant, whilst the others (19 plants) were similar in habit of growth to the common Bottle-brush (*C. citrinus,* syn. *C. lanceolatus*). The leaf characters of the latter were also more closely akin to

those of *C. citrinus* in shape and in venation character. The colour of the filaments of both parents as well as the hybrids was scarlet or pale crimson, so that no notes were made. It is noteworthy, however, that spikes of the F_1 generation were fully $1\frac{1}{2}$ to 2 inches longer than the flowering spikes of the parent plants.

It will be seen that these experiments with "Soy Bean", "French Bean" and Scarlet Bottle-brush, like many other experiments in plant breeding, have demonstrated the phenomenon of segregation, and that the presumed stable biotypes or elementary (micro) species were produced when crosses were made between parental plants which may be regarded as unstable heterozygotes. In each case there were two kinds: homozygotes and heterozygotes. The pea-green "Soy Bean" and the white-seeded "French Bean" proved to be stable biotypes. I was unable to carry on the experiments with *Callistemon* beyond the F_2 generation, but have no doubt that the results would have been the same, as numerous seedlings have been raised and distributed by nurserymen from the second generation plants, and these seedlings show characters in the shape and venation of the leaves similar to those of some of the F_2 generation (parent plants) and are quite distinct from those of *C. acuminatus* and *C. citrinus*.

The evidence in connection with these experiments shows that pure bred races of plants can be produced as to colour of the seed-coats of "Soy Bean" and "French Bean" and as to venation and shape in the leaves of *Callistemon*. It also shows that in homozygous forms, races, genotypes, biotypes or whatever name we like to call them, these factors or elements are evidently sorted out in an orderly fashion. In heterozygous forms or

races it is otherwise. It is in connection with the latter that the systematists have to think in terms of biological problems, for we are reminded by Du Rietz (1930, p. 352) "that heterozygotes will produce homozygotes, but not the reverse".

The Biotype.

It would appear from recent discussions that the term biotype (which, according to Johannsen, 1909, and Du Rietz, 1930, is defined as a population consisting of individuals with identical genotypical constitution) is now generally accepted in preference to the term "genotype" as originally understood. According to Du Rietz (1930, p. 341), a biotype may be either homozygous or heterozygous, and that there is probably not much chance of finding completely homozygous biotypes in populations other than strictly autogamous ones. This means that the only really homozygous biotypes existing will be those forming pure lines.

In a series of papers published in the years 1912-1916, Lotsy claimed that the homozygous biotypes were the real fundamental units of taxonomy, and therefore the units worthy of being called species, but in a more recent work Lotsy (1925, p. 27) receded from this belief, doubting even the existence of any absolutely homozygotic biotypes in nature as well as in pure lines. In a postscript Du Rietz (1930, p. 427) draws attention to a paper published by Nilsson (1930) in which he has found "that different individuals of a certain so-called 'pure line' of oats produced pure lines differing considerably in their production of 'mutations', some of them giving a much higher percentage of mutations than others. From this result Nilsson draws the conclusion that the original

'pure line' did not contain only homozygous individuals, this being no pure line at all, and that the mutations appearing in it (and in analogous false pure lines) are no real mutations, but simply some sort of 'segregants' caused by the heterozygosity."

In commenting on this, Du Rietz states: "This certainly does not speak in favour of the current theory of the rapid production of pure (*i.e.,* homozygotic) lines by autogamous reproduction. On the contrary, it gives a strong support to Lotsy's recent doubting of the existence of any absolutely homozygotic biotype in nature, even in pure lines. This implies that the existence of real pure lines in nature may be a mere illusion that the taxonomical importance of the pure line-concept thus would be still smaller than postulated." Du Rietz's (1930, pp. 338-339) remarks were based on the definition given by Johannsen (1903): "A pure line is a population consisting of the individuals born by strictly autogamous reproduction of one homozygotic individual."

When thoroughly analysed, it will be seen that a race or pure line is pure if it breeds true and not otherwise, and can only be produced by the union in fertilisation of two germ cells which are alike in the factors they bear. The factor may confer tall or dwarf characters, colour, shape, hairiness and probably also elements of physiological or chemical importance. We have abundant evidence that certain plants are indistinguishable in morphological characters, whilst, on the other hand, they may be readily separated according to the composition of the respective essential oils or physiological characters.

Mueller's remarks on the Eucalypts of the "North Australian Expedition" in 1856 are most interesting, as will be seen from the following observations:

"The Stringy-bark tree of this part of the country (*E. tetradonta*) differs from the southern species, and although a Eucalyptus, it produces, angophora-like, a four-toothed calyx. Several other species of this genus, all trees, were noticed, of which two are highly ornamental in producing scarlet flowers and lamellar bark, another in having a double operculum. I found it necessary, for the sake of satisfactory distinctions, to describe all the tropical Eucalypti (nearly thirty species) on the spot, and I was never at a loss how to discriminate between variety and species by considering *all the characters of the trees collectively*, and paying due attention to the soil, habit, structure and texture of the bark, the manner of its decortications; consulting likewise, as very important, the insertion and form of the fruit-valves, which, before opening, form either a flat or more or less convex vortex to the capsule, a character which, beautiful as it is, can only be studied in living plants. Important also are the structure and form of the fertile seeds, most of the ovules becoming abortive; the former are, in many kinds, provided with a very large wing, although the seeds of the generality of the species are wingless. As precisely by the same character *Fabricia* is separated from *Leptospermum,* I do not hesitate to refer the former, as a subgenus, to the latter."

The late Mr. Maiden,[1] in commenting on the above, states: "What does all this lead to? To the fact that the conception of a species is based on empiricism, and that therefore we must rely upon human judgment in apportionment of a sufficient amount of variation to constitute a species. And in all cases in which we rely upon human judgment we have the potentiality of human error.

[1] Unpublished manuscript.

"Although endless fun can be poked at the illogical positions in which we sometimes find ourselves by our conception of species, it is idle to attempt to abandon them, for plants will be labelled species on the evidence of our senses to the end of time.

"With more intelligent ideas of the value of types, increased attention has been given, in recent years, to their preservation. A type is the only thing about a species that is fixed; it is a botanical lighthouse, and many men have suffered botanical shipwreck because they argued about a plant which they deemed or assumed to be the type and which was not so. What harm authority has done in this connection, particularly in Australia! A botanist has written about a plant, and we, unwarrantably assuming in a particular case that he has had access to the type, follow him, and stray even further from the path.

"So important is the matter of types that a certain amount of terminology is gathering, and instead of being content with types and co-types, we have now nerotypes, clastotypes, clonotypes, spermotypes and even other terms in this connection.

"Situated as we are in Australia with our types taken to the end of the world (for more than half a century), Mueller being the first resident botanist who checked this hitherto necessary state of things, it is often very difficult to obtain access to authentically named material. I am stating the facts as they are, not unfavourably commenting upon them, for if the early types had not been taken care of in the British Museum and other great herbaria, I shudder to think what would have become of them. During the last few years there has been a recrudescence of botanical expeditions to Australia

organized in Europe, and if only for the reason that visiting botanists have always been given facilities for work in Australia, I trust that they will reciprocate to the extent of seeing that specimens of their types are made available in some part of this continent.

"Personally I have always been treated considerately by the keepers of the great herbaria in my search for types of this genus, but because the difficulty of dealing with specimens at the other end of the world is naturally so great it is in the interests of science that we should put as many bridges across the space as possible."

Conclusion.

In concluding this brief review, I have endeavoured to bring before you a few of the difficulties with which systematists are confronted. The technique of the older school of botanists is admittedly formidable, and we are now faced with a deluge of technical methods of classification from the modern school of genetics. The torrent of literature on the subject increases year by year, so much so that we are reminded of that old adage of Lock, who tells us: "A man may find an infinite number of propositions, reasonings and conclusions in books of metaphysics, schools of divinity and some sorts of natural philosophy, and after all, know as little of God, spirits or bodies as he did before he set out."

The same line of reasoning may be used in connection with certain discussions concerning those invisible things in the realm of genetics and certain diseases of plants, as, for example, the so-called "ultra microscopical organism of the Banana", commonly known as "Bunchy Top". It might be wise to refrain from using such terms until we know something more definite about the cause of such

troubles, and are better able to cope with them; otherwise we may find ourselves classed in the same category as Lewes' declaration concerning philosophy, which he regarded as "a desert, whose only semblance of vegetation is a mirage—the desert without fruit, without flower, without habitation and without horizon; arid, trackless, silent, but vast, awful and fascinating", adding that "if we understand by Philosophy what all philosophers consider it—metaphysics—then to attempt to construct a science of metaphysics is an impossibility".

Our province as systematists is not in the mysterious labyrinth of mental speculations. We have innumerable characters visible to the naked eye which can be used with advantage when foraging in the fields of natural history research.

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THE MITOTIC ACTIVITY OF NORMAL AND MALIGNANT TISSUES AND ITS MODIFICATION BY X RAYS.

A Bio-Physical Study.

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(With Plate I and twenty-four text-figures.)

(Read before the Royal Society of New South Wales, June 1, 1932.)

Preface.

In this paper I have presented the results of a physical and mathematical study of the mitotic activity of normal and malignant tissues and the modifications produced in that activity by the action of X rays. It has been my aim to give a concise statement of the facts and theories in the most straightforward way, and in arranging the sequence of the various sections I have disregarded to some extent the order in which the investigations were made.

This research, for the purpose of which I was granted leave of absence from the University of Sydney and partial support from the Cancer Research and Treatment Fund of that University, was carried out at the Strangeways Research Laboratory, Cambridge, and

l'Institut du Radium de l'Université de Paris, during my tenure of a Rockefeller Foundation Fellowship. The investigation was completed at the Strangeways Research Laboratory with the aid of a grant from the Medical Research Council.

It is a pleasure to acknowledge my indebtedness to Dr. A. E. Barclay, Lecturer in Radiology in the University of Cambridge, for his help and guidance; to Dr. H. B. Fell, Director of the Strangeways Research Laboratory, for instruction and critical advice in the tissue culture section of the investigation; to Mr. F. G. Spear, Radiologist in the Strangeways Research Laboratory, for advice and many valuable suggestions; to Mr. S. W. P. Steen, of Christ's College, and Professor F. Holweck, of l'Université de Paris, for advice and criticism in the analytical section of the work; to Professors C. Régaud and A. Lacassagne, of l'Institut du Radium de l'Université de Paris, for guidance and criticism in my studies of malignancy; to Dr. J. Chadwick, of the Cavendish Laboratory, for the loan of apparatus and measuring instruments and to Mr. V. C. Norfield, Assistant in the Strangeways Research Laboratory, for co-operation in the preparation of routine cultures.

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THE MITOTIC ACTIVITY OF JENSEN'S RAT SARCOMA AND ITS MODIFICATION BY X RAYS.

Introduction.

The discoveries of the Roentgen ray (1895) and radium (1898), and the development of the electronic theory of matter, revolutionised the attitude of the physicist towards biology, and of the biologist towards physics. The new outlook on physics provided the basis, and to some extent determined the lines along which modern biophysics has developed.

The nature of life itself, however, still eludes us, and we can only study the way in which it is influenced by various physical forces and agencies.

Radiations are physical forces, that can be measured and expressed in mathematical terms; they have a marked influence on living cells, and constitute a suitable instrument for the investigation of the problems of living matter. Just as radiations have elucidated the structure of the atom, so they may perhaps reveal the basic features of vital processes.

The effects of radiations on living cells have been studied and applied in the treatment of pathological conditions in man, for it was found that they sometimes had a beneficial influence. The treatment of disease commenced and continued on empirical lines, guided by experience. Many and diverse theories have been advanced, but little is known as to the manner in which the rays act on the living cell, or why they have, apparently, a selective action in certain conditions.

The study of the effects of radiations on the living cell grown in culture (*in vitro*) is a promising method for attacking many radiological problems, and has already yielded results of importance. The tissue culture method is of great value, because it enables us to

eliminate many secondary factors due to the physiological activities of the body as a whole, and to determine how the cells themselves react.

The work which follows deals with my own experiments, which were concerned with a study of mitotic activity in tissue cultures of normal fibroblasts, and Jensen's rat sarcoma (*in vivo*), and with the modifications produced in the mitotic activity by X rays. I have made use of the mathematical method to reproduce the results of hypotheses in a form more suitable for comparison with experimental results, and, in one instance, to suggest lines of experimental research. It is necessary, however, to bear in mind the possibility of error that may be introduced if too much reliance is placed on a purely mathematical outlook on biological problems. The factor of life, for which as yet we cannot find a place in our formulae, may play an unsuspected part.

Part I.

The Mitotic Activity of Tissue Cultures and its Modification by X Rays.

1. *The Statement of the General Problem.*

The experiments to be described were undertaken in order to study

(*a*) the precise significance of the time of administration of a given dose of X radiation in the determination of the quantitative biological reaction;

(*b*) the mechanism of the disappearance of mitoses from irradiated tissue cultures;

(*c*) the variation of the radio-sensitivity of a cell, according to its functional state;

(*d*) the effect of small doses of X radiation on mitosis, with special reference to the possibility of stimulating a tissue to increased activity.

My work has revealed the existence of an intimate relationship between these apparently independent investigations. I have accordingly decided to consider the problem as a whole rather than in separate parts. The experimental work has therefore been presented in various sections, each section making an independent contribution to two or more sub-sections of the general problem.

2. *Previous Work.*

It has not yet been possible, through clinical or laboratory studies, to determine whether, in the X ray treatment of malignant tumours, the best results are obtained by the use of a brief irradiation of great intensity or a protracted irradiation of small intensity.

The only comparative clinical statistics that I can find are those of Laborde,[1] which are gathered from various sources and relate to radium-treated cancers of the uterus. Laborde concludes that there is not much difference in the results obtained by the use of the "massive" or the "protracted" technique.

The studies of Krönig and Friedrich[2] were largely instrumental in establishing the "intensive" treatment of malignant tumours; from Germany this view gained ground throughout the world, but the method was always more extensively used in Germany than elsewhere. It is notably the French who were the pioneers of the "protracted" method of treatment, and the views of Régaud are now widely recognised.

The subject has been studied in the laboratory by many people; from the vast literature I will note a few of the more important works.

Holthusen[3] studied the effects of X radiation on the eggs of Ascaris and obtained a less effect with less intensity.

Lazarus-Barlow[4] showed that a given dose of radiation was more destructive to the rectum of the rat when a large intensity factor was employed.

Arntzen and Krebs[5] studied this effect on sprouting peas, and were able to demonstrate a decrease in the biological effect when the intensity of the radiation was decreased.

Matoni,[6] working with sprouting beans, and Suzanne Ancel,[7][8] working with sprouting lentils, found similar results.

The problem has been investigated on tissue cultures by Canti and Spear,[9] who found a less effect from radium treatment with decreased intensity than one would expect according to physical calculations.

Russ and Scott[10] introduced radon capillaries into Jensen's rat sarcoma and the liver of rats; the effect on the liver was found to be almost independent of the intensity. Only when the difference in intensity was very marked did the smaller intensity have relatively smaller effect.

The latest contribution to the question has been made by Juul.[11] Juul employed white mice, bearing transplanted sarcoma and adenocarcinoma; the experiments were evidently very carefully conducted and the results indicate that the distribution of a dose of radiation (X and γ rays) over a longer time gives less effect than the same dose administered in a short time.

In certain experiments on the effects of β rays on mitosis in Jensen's rat sarcoma, Mottram, Scott and Russ[12] found that 180 millicuries of radium emanation acting for 30 seconds gave the same mitotic changes as did 30 milligrams of radium salt in 30 minutes. This result has been interpreted by Juul[11] as indicating a stronger effect from the greater intensity. I do not agree with Juul in this interpretation and I have discussed the matter in the section of this work relating to Jensen's rat sarcoma.

Lazarus-Barlow,[13] working with radium emanation and the eggs of Ascaris, Wood and Prime,[14] who irradiated tumour cells, Packard,[15] working on Drosophila, Glocker,[16] who irradiated beans, and Laser,[17] who studied the inhibition of growth in tissue cultures irradiated with the β and γ rays from mesothorium, have shown that within the limits of their experiments, alteration in the time and intensity factors have no significance in the determination of the biological reaction to a given dose of X rays.

The very recent experiments of Langendorff[54] have likewise shown that the injury to the germ cells of the sea urchin was proportional to the X ray dose.

Redfield and Bright[18] studied the thickening of the membrane on the irradiated eggs of *Nereis limbata*; they found the greatest effect with the smaller intensity for a longer time.

Zuppinger[19] studied irradiated eggs of Ascaris and, even though his experimental material was the same as that employed by Holthusen,[3] he arrived at opposite conclusions.

The most significant and best known experiments in this regard are those of Régaud.[20] In 1922 Régaud

carried out a series of particularly interesting experiments in which he employed the testes of rams. As a result of this work and his later work[21] on the testicle of the rabbit, Régaud concludes that the radiation time is a more important factor than the size of the dose, and that protracted irradiation is more effective than intensive irradiation. He has also studied the problem of "splitting" the dose into various fractions, and has pointed out that, unless the dose is fractionated, it is impossible to bring about the total and complete sterilisation of the testicle without producing lasting damage to the teguments of the rectum.

Schinz and Slotopolsky[22] have made similar experiments with the testes of rabbits and obtained the same results.

The results obtained from these experiments on increased time factor and "split dosage" have been explained on the assumption that the cells are most sensitive to radiation during the mitotic period. This conclusion leads us to a consideration of another aspect of the general problem, namely, the variation in radiosensitivity of a cell according to its functional state.

Régaud[20] emphasises the importance of irradiating all the cells in their most sensitive state—the stage of cell division. For this purpose it is necessary to make the irradiation period long enough for the majority of the cells to pass through this stage. Régaud points out that there is no need of great intensity because such cells are relatively easy to destroy.

Bergonier and Tribondeau,[23][24] Régaud and Blanc,[25] and Krause and Zeigler[26] showed that the most rapidly proliferating tissues are most radio-sensitive. From this

observation they also concluded that cells are most readily destroyed during mitosis.

I would like to point out here that this interpretation of a now very well known principle is not the only possible one. If the sensitive state was "pre-mitotic" we would still find the most rapidly proliferating tissues to be most sensitive to radiation.

Richards,[27] Grasnick,[28] Holthusen,[29] and Alberti and Politzer,[30][31] working on ova and tissues from cold-blooded animals, support the view that the cell in division is most sensitive to radiation.

Mottram[32] irradiated the ova of Ascaris and the root tips of seedling beans; he found that (1) the dividing ova of Ascaris are at least eight times as vulnerable as resting ova, and (2) the most vulnerable stage in division is the metaphase.

Langendorff[54] showed that in the irradiated germ cells of the sea urchin the maximum injury takes place immediately after impregnation, decreases slowly, reaches a minimum during the metaphase and increases again with the anaphase.

Strangeways and Hopwood,[33] on the other hand, carried out certain quantitative experiments with irradiated tissue cultures, and by direct observation found that the decrease in the number of cells in mitosis was due to an inhibition of the onset of mitosis, and not due to the disintegration of cells whilst actually passing through mitosis.

This conclusion is supported by Kemp and Juul,[34] who used tissue cultures, and Ancel and Vintemberger,[35] who irradiated whole chick embryos. These latter experiments have been vigorously criticised by Régaud and Lacassagne.[36]

During recent years several studies have been made on the course of mitosis after irradiation. On the whole, the results agree in showing a gradual disappearance of normal mitotic figures from irradiated tissues, followed after a time by a reappearance of large numbers of mitoses, many of which are, however, abnormal.

Lacassagne and Monod[37] studied this problem on uterine cancer after radium treatment and on dog sarcoma after X radiation. They found that the mitoses were affected at once, and disappeared within a very short time. After some time the mitotic figures began to reappear; they became more and more frequent but were all degenerate.

These results are in fair agreement with those of Alberti and Politzer,[30][31][38] who conducted experiments on the X rayed cornea of salamander larvae.

Stoel[39] studied the action of radium radiation on normal mouse skin and tar carcinoma; he found minor differences in the mitotic changes produced in these two tissues, but the general effect was the same.

Mottram, Scott and Russ[12] found similar changes in Jensen's rat sarcoma even after large radium doses.

The finding has also been confirmed by Régaud,[40] who used chick embryos, and Dustin[41][42] in his investigations on cancer of the uterus after radium treatment.

In tissue cultures Canti and Spear[43] studied the same problem and under certain conditions found that the subsequent increase in the number of mitoses exactly compensated for the initial fall.

Kemp and Juul[34] have performed what appears to be the same experiment, but have failed to find any significant increase in the mitoses above normal.

This brings us to a further consideration of the very extensive literature on the stimulating effects (transitory or otherwise) of small doses of radiations.

The term stimulating dose plays an important rôle in the earlier works on radiotherapy; the fear of stimulating the cancerous cells to more rapid growth played some part in the development of the "intensive" treatment of malignant growths.

Gilman and Baetjer[44] studied the effects of small doses of X radiation on the development of the chick, and under certain conditions were able to produce an accelerated development. They obtained a similar result in their experiments on the eggs of Amblystoma.

Lazarus-Barlow and Bonney[45] experimented upon the eggs of Ascaris and came to the conclusion that X rays and the radiations of radium, thorium, and uranium, possess two distinct properties. They may either favour or hinder cell division and are capable of acting independently on the ova in either manner.

Lazarus-Barlow and Beckton[46] found that small doses of γ and the hardest β radiation from radium induce an initial acceleration in the rate of cell division in the ova of Ascaris; this was followed by a progressive retardation of the development.

Hastings, Beckton and Wedd[47] showed that the rate of hatching out of silkworms could be increased by irradiation, and Markovits[48] showed that in paramoecia the first division following exposure to mesothorium was usually delayed, but the following divisions were accelerated.

Kimura[49] found that while the growing power of mouse sarcoma was stimulated by small doses of X radiation, mouse carcinoma was not appreciably affected.

Laser,[17] in the experiments already quoted, occasionally noted a temporary increase of growth in irradiated tissue cultures.

Falta and Schwarz[50] observed an accelerated rate of growth in irradiated oats, but Schwarz, Czepa and Schindler[51] found no increase in the growth rate of irradiated seedlings.

Arntzen and Krebs[5] were able to demonstrate the existence of an absolute stimulatory effect in the Victoria pea, but Wigoder and Patten[52] failed to find any evidence of increased activity in irradiated bean-roots.

The latest contribution to the subject has been made by Miss Goulston.[53] Miss Goulston irradiated the chorio-allantoic membrane of a ten-day chick embryo by making a window in the shell. Radium tubes with active lengths of 1 cm., with 0·5 mm. gold-platinum or 0·5 mm. platinum filter, containing from 2 to 5 mg. of radium element, were laid across the window without actually touching the membrane. After irradiation from 2 to 5 hours and subsequent incubation for three days, macroscopic examination revealed irregular thickenings; microscopic examination revealed in some cases marked hypertrophy of the mesenchyme.

This appears to afford undoubted evidence of a hypertrophic reaction to radiation, and, therefore, of a stimulating effect of the rays.

This short review serves to illustrate the diversity of opinion that still surrounds some of the fundamental problems of radiological research.

In my opinion this is due, at least in part, to lack of information concerning the normal mechanism of the

various biological reactions used to determine the effect of any given treatment.

Further, the employment of heterogeneous radiation makes the accurate determination of the conditions under which any particular biological reaction occurs more difficult. The already complex nature of the biological material demands the maximum simplification of the physical conditions.

So far, nobody has studied the inter-relation between the various phenomena, in the determination of the biological reaction to a given treatment. I believe that it is not possible to comprehend fully the significance of the time factor, for example, without having at our disposal certain information relating to

(*a*) the variation in the sensitivity of a cell according to its functional state;

(*b*) the mechanism of the action involved in the disappearance of mitoses from irradiated tissue cultures.

I have, therefore, attempted to study the whole problem from a different point of view, and the object of this investigation is essentially an analytical one.

The work was begun by investigating the mechanism of the particular biological phenomenon that I proposed to employ as quantitative indicator of reaction, namely, mitotic activity in tissue cultures.

I have also simplified the physical conditions of experiment by using a beam of approximately homogeneous radiation.

Section 1.

The Occurrence of Mitosis in Tissue Cultures.

1. General Ideas.

In any quantitative research into the problems of radiotherapy we are obliged to choose some indicator to measure the amount of biological change induced by a given "dose" of radiation, and the advantages of employing mitotic activity as indicator are:

1. The cell is particularly vulnerable to radiations of various wave length, before passing into the stage of recognisable mitosis.[1]

2. The dividing cell has a distant significance in all growth phenomena.

In a tissue culture *in vitro* increase in volume of the implanted fragment may be due to one or all of the following causes:

(*a*) Multiplication of the cells by mitotic division.
(*b*) Formation of intercellular substance which does not form an integral part of the cells.
(*c*) Hypertrophy of individual cells.

In normal cultures it is chiefly due to cellular multiplication by mitotic division.[(55)] The rate at which cells migrate from the implant depends upon several factors, and the subsequent history of an individual cell depends very largely on the conditions of its environment. Under favourable conditions the cell which has wandered out remains in the vegetative state for a certain length of time, reaches maturity, and divides, the daughter cells passing into the vegetative condition.

This process is repeated[(56)] until the culture medium is so modified by the products of cellular metabolism that the conditions for growth are no longer favourable. At

[1] This statement refers particularly to fibroblast cells in tissue cultures (see subsequent sections). It is not necessarily true, in general (see "Previous Work", page 61).

this stage the rate of growth begins to decrease and sooner or later reaches zero.

It has not been shown, however, that all growing cells after attaining maturity will necessarily enter mitosis. A cell may show amoeboid movement followed by reproduction; it may migrate and remain in the vegetative state. Some workers claim a third possibility, *i.e.,* fission accompanied by amitotic division of the nucleus. In the present analysis it has been assumed that a constant fraction λ of the vegetative cells that have attained maturity will enter mitosis.

The average time spent by a cell in the vegetative state is large compared with the time spent in the dividing state. The precise determination of these times presents considerable difficulties, owing to the fact that the commencement of prophase and termination of telophase are not always sharply defined. In this study average figures of ten hours and half an hour respectively have been used, these figures being based on the observation of several workers.[57] [58] [59] [60]

By studying local occurrence of mitosis in the peripheral zone of a growing culture of fibroblasts, Fischer[58] observed that cell divisions appeared to occur periodically. "It is conceivable to explain the phenomenon", he says, "as the result of a controlled action from several of the neighbouring cells with which the cells, about to divide, are in direct contact." In other words, we are dealing with a partial organism and not with independent cellular individuals. Fischer found that on an average 2% of cells of a tissue culture are in mitotic division at a given moment.

When the whole zone of outgrowth is considered, Spear[61] has observed that the total number of cells in

mitosis remains fairly constant and that, if mitosis is plotted against time, the resulting curve rises to a maximum value in about eighteen or twenty hours, remains fairly constant during the succeeding twenty-four hours, and then falls away.

These two results are not inconsistent, because when dealing with the culture as a whole we are observing the integrated effects of the mitotic pulses described by Fischer.

2. General Theory of the Occurrence of Mitosis in Tissue Cultures.

If N = number of cells in zone of outgrowth at time t,
T = average time spent in vegetative state,
T_1 = average time spent in dividing state,
λ = that fraction of the total number of mature cells which enter mitosis,
n_t = number of mitotic figures present at any instant in an individual culture,

then, in general, we may write

$$N = f(t).$$

The number of cells produced in the zone of outgrowth in the interval of time dt after time $t = t_1$ is given by the relation

$$dN = f^1(t_1)dt,$$

and these cells, or a constant fraction of them, λ, will, after growing to maturity, enter the dividing stage at time t given by the relation

$$t = t_1 + T.$$

That is to say the curve representing the rate at which cells are entering mitosis follows closely the gradient of the curve representing the rate of production of new cells

in the medium, but is displaced along the axis of time to the extent of T hours.

It follows that

$$n_t = \int_{t-T-T_1}^{t-T} \left(\frac{dN}{dt}\right) dt,$$

and in general this reduces to the relation

$$n_t = \lambda\{N_{t-T} - N_{t-T-T_1}\}$$

If over a range of time, expressed in hours, $\left(\frac{dN}{dt}\right)$ and t are mutually independent then

$$n_t = \lambda \left(\frac{dN}{dt}\right)_{t=t_1} T_1$$

where t_1 is contained within the range. Since T_1 is approximately half an hour, we can write

$$n_{t=t_1+T} = \frac{\lambda}{2}\left(\frac{dN}{dt}\right)_{t=t_1}$$

3. Application of General Theory.

In order to apply the general theory to particular cases it is necessary to know something about the function f(t). The only way in which this problem can be approached is to make determinations of the relative rate of increase of area of the implanted tissue fragment. From observations on this rate of increase, "growth-rate curves" can be constructed, but it is not certain that they actually represent the rate at which new cells are being produced in the zone of outgrowth. Ebeling,[62] however, maintains that the thickness of the zone of new tissue remains reasonably constant, and that the rate of growth can be taken to be practically identical with the rate of increase of area, an observation which leads to interesting

results in the application of the general theory to particular instances.

If the relative increase in area (A) of the zone of outgrowth in a culture is plotted against time, curves are obtained as shown in Figure 1, and such curves can be represented by a relation of the form:

$$A = M(1 - e^{-\alpha t})^2$$

where M and a are constants.

If N = number of cells in zone of outgrowth at time t,

K = constant, directly proportional to area of implanted tissue fragment,

we may write

$$N = K(1 - e^{-\alpha t})^2$$

From this it is seen that

$$\frac{dN}{dt} = 2\alpha K(e^{-\alpha t} - e^{-2\alpha t})$$

and it is clear that $\frac{dN}{dt}$ rises from zero through a maximum value $\frac{1}{2}aK$ corresponding to time

$$t = \frac{1}{\alpha}\log_e 2$$

and then falls away to zero, and in the vicinity of the point of inflexion of the growth rate curve $\frac{dN}{dt}$ is sensibly constant. It is seen also that the mitosis-time curve rises from zero, attains its maximum value after time t given by

$$t = \frac{1}{\alpha}\log_e 2 + T$$

and in the vicinity of this maximum the mitosis-time curve is sensibly flat. Ultimately the curve falls away to zero.

4. Condition for Mitotic Comparability of a Series of Culture Groups.

For an individual culture we have

$$n_{t=t_1+T}=\frac{\lambda}{2}\left(\frac{dN}{dt}\right)_{t=t_1}$$

and for a group of cultures

$$\Sigma n_{t=t_1+T}=\frac{\lambda}{2}\Sigma\left(\frac{dN}{dt}\right)_{t=t_1}$$

and it becomes clear that different groups of cultures from the same batch will each contain the same number of dividing cells if

$$\lambda\Sigma\left(\frac{dN}{dt}\right)=\text{constant.}$$

throughout these groups.

If we now assume that the relative rate of increase of area of a culture is independent of the size of the implanted tissue fragment, then for cultures prepared under any given conditions

$$\frac{dN}{dt}=2\alpha K\Phi$$

where Φ is the constant for the straight line portion of the growth rate curve.

Thus

$$\lambda\Sigma\left(\frac{dN}{dt}\right)=2\alpha\lambda\Phi\Sigma K$$

and different groups of cultures will be mitotically comparable over the range determined by Φ if

$$\Sigma K = \text{constant}$$

for each culture group.

This means that the total implanted area of each group of cultures must be constant.

Further, it follows that if we represent the area of the zone of outgrowth of an individual culture by a, comparison of one group of cultures with another is conditional upon

$$\Sigma a = \text{constant}$$

for each group of cultures.

Subsequent work will show that the above condition for mitotic comparability is essential, but not necessarily sufficient.

Let us now make some observations on the relative rates of increase of area of a series of cultures prepared under identical conditions.

5. Experimental.

The tissue used for cultivation was obtained from the choroid and sclerotic of chick embryos. The tissue fragments were grown on coverslips in a medium consisting of equal parts of fowl plasma and chick embryo extract and cultures of the second passage only were employed.

Tissue fragments of various sizes were used and these were placed in the centre of the culture medium which, in each case, was spread out into a circle of the same size. This operation was readily performed by placing under the coverslip a sheet of paper on which was traced a circle of the required diameter. The area of the zone of outgrowth at any time could be determined with the aid of a camera lucida and planimeter.

An example of the results obtained is given in Table 1, in which is shown the total area A_1 of the implanted fragment and the relative increase in area after various lengths of time from the commencement of incubation.

TABLE 1.

	0 hrs.	15 hrs.	$26\frac{1}{2}$ hrs.	$46\frac{1}{2}$ hrs.	55 hrs.
Culture A ..	0·100	2·00	6·08	15·57	17·00
Culture B ..	0·139	2·00	6·35	10·90	11·60
Culture C ..	0·115	2·00	6·35	13·00	14·40

These figures are plotted as curves in Figure 1.

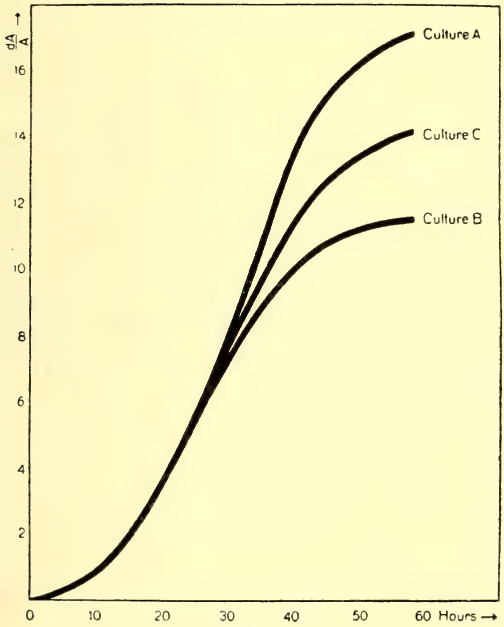

Fig. 1.

6. Discussion.

It is clear that in these preparations the rate of increase of area of a tissue fragment is not independent of the size of the implanted fragment. The rates of increase of pieces of tissue of approximately the same

size are distinctly comparable over the straight line portion of the curves, but experiment shows that the differences become aggravated with the variation in size of the original explant. The variation is almost certainly nutritional in origin. It is obvious that the complete independence of relative rate of increase of area and size of implant would demand an infinite medium.

It is seen that the growth curves are tending to become linear after about fifteen hours, and thus the mitosis curve becomes sensibly steady after about twenty-five hours and remains so for approximately a further fifteen hours.

Spear has found that it is practicable to make comparative use of mitotic counts in different groups of cultures provided they are used between the eighteenth and fortieth hour from explantation (second passage), and from mathematical considerations the steadiness of the mitosis curve would appear to be maintained for a few hours on either side of a point midway between the limits mentioned by Spear.

It can be shown that

$$\alpha = \frac{\frac{d}{dt}\sqrt{A'_1} - \frac{d}{dt}\sqrt{A'_2}}{\sqrt{A'_2} - \sqrt{A'_1}}$$

where A'_1 represents the area of the zone of outgrowth at time t_1. The $\sqrt{A'}$ curve for culture B has been plotted in Fig. 2, and it has been determined that

$$\alpha = 0{\cdot}03 \text{ (approximately)}$$

when t is expressed in hours.

The maximum value of the mitotic count is seen to occur at a time t given by the relation

$$t = \frac{1}{\alpha}\log_e 2 + 10$$

and substituting the above value of a we find that

$$t = 33 \text{ hours (approximately)}.$$

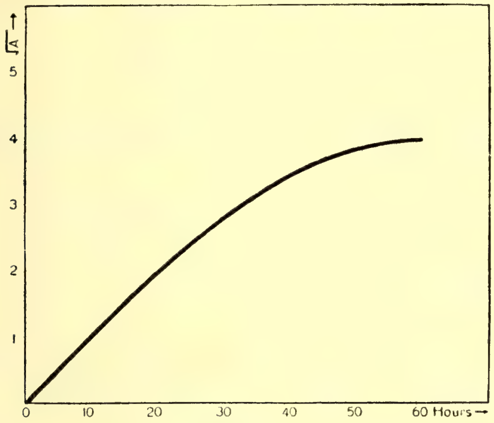

Fig. 2.

7. The Average Frequency of Mitosis.

It has already been mentioned that the average frequency of mitosis in the peripheral zone of outgrowth has been determined by Fischer as about 2% of the total cells present. A theoretical determination of the upper limit of the average frequency of mitosis in the whole zone of outgrowth can be determined from the general theory.

We have

$$N = K(1 - e^{-\alpha t})^2$$

$$\frac{dN}{dt} = 2\alpha K(e^{-\alpha t} - e^{-2\alpha t})$$

and the maximum value of $\frac{dN}{dt}$ occurs at time t and is given by the equation:

$$e^{-\alpha t} = \frac{1}{2}$$

If we assume that all the mature cells enter mitosis $(\lambda = 1)$ we obtain an upper limit to the average frequency of mitosis, and in this case the number of dividing cells present at time

$$t = t_1 + 10$$

will be given by $\frac{1}{2}\left(\frac{dN}{dt}\right)_{t=t_1}$. If the average value of $\frac{dN}{dt}$ over the range of time t_1 to t_2 be represented by

$$\left|\frac{dN}{dt}\right|_{t_1}^{t_2}$$

we have

$$\left|\frac{dN}{dt}\right|_{t_1}^{t_2} = 2\alpha K\left\{\frac{1}{(t_2-t_1)}\int_{t_1}^{t_2} e^{-\alpha t}dt - \frac{1}{(t_2-t_1)}\int_{t_1}^{t_2} e^{-2\alpha t}dt\right\}$$

$$\left|N\right|_{t_1}^{t_2} = K\left\{1 - \frac{2}{(t_2-t_1)}\int_{t_1}^{t_2} e^{-\alpha t}dt + \frac{1}{(t_2-t_1)}\int_{t_1}^{t_2} e^{-2\alpha t}dt\right\}$$

If we consider a range of time 2 Φ in the vicinity of maximum mitosis then we may write

$$t_2 = \frac{1}{\alpha}\log_e 2 + \Phi$$

$$t_1 = \frac{1}{\alpha}\log_e 2 - \Phi$$

and the corresponding time limits for the curve giving the total number of cells present in the zone of outgrowth are then seen to be given by

$$t_2 = \frac{1}{\alpha}\log_e 2 + \Phi + 10$$

$$t_1 = \frac{1}{\alpha}\log_e 2 - \Phi + 10$$

and it is clear that

$$\frac{\frac{1}{2}\left|\frac{dN}{dt}\right|_{t_1}^{t_2}}{\left|N\right|_{t_1+10}^{t_2+10}} = \frac{\left|n\right|_{t_1+10}^{t_2+10}}{\left|N\right|_{t_1+10}^{t_2+10}}$$

Further, it can be shown that

$$\frac{\left|n\right|_{t_1+10}^{t_2+10}}{\left|N\right|_{t_1+10}^{t_2+10}} = \frac{\frac{\alpha}{2}\left\{\frac{\text{Sin h } \alpha\Phi}{\alpha\Phi} - \frac{1}{2}\frac{\text{Sin h } 2\,\alpha\Phi}{2\,\alpha\Phi}\right\}}{1 - e^{-10\alpha}\frac{\text{Sin h } \alpha\Phi}{\alpha\Phi} + \frac{e^{-20\alpha}}{4}\frac{\text{Sin h } 2\,\alpha\Phi}{2\,\alpha\Phi}}$$

and when $\alpha\,\Phi$ is small this reduces to

$$\frac{\frac{1}{4}\alpha}{1 - e^{-10\alpha} + \frac{e^{-20\alpha}}{4}}$$

substituting the value

$$\alpha = 0{\cdot}03$$

we see that the upper limit to the average frequency of mitosis is of the order of 1·5%. This result is of particular interest in so far as it is of the same order of magnitude as the figure determined by Fischer for the frequency of mitosis in the peripheral zone of cultures, where the conditions for growth are most favourable.

In general the values of α are such that $\frac{e^{-20\alpha}}{4}$ can be neglected in comparison with $e^{-10\alpha}$ and the ratio

$$\frac{\left|n\right|_{t_1+10}^{t_2+10}}{\left|N\right|_{t_1+10}^{t_2+10}}$$

reduces to 2·5%.

8. The Preparation of Comparable Groups of Cultures.

For the successful preparation of comparable groups of cultures it is necessary that the following conditions should obtain:

(*a*) The fragments of implanted tissue should all be of the same size.

(*b*) Equal amounts of culture media should be used in the preparation of each culture.

(*c*) The media should be spread into circles of the same area with the tissue fragment in the centre of the circle.

(*d*) Each experimental culture should be checked by a corresponding control; such a "pair" being made from the bisection of a single piece of tissue of an earlier subcultivation. By this means it is possible to eliminate the introduction of errors due to inherent variation in the explanted tissue.

Such cultures after twenty hours' incubation should all show a zone of outgrowth of equal size. Any unhealthy cultures can be seen at a glance and are readily eliminated.

9. Conclusions.

1. In tissue cultures, the rate of increase of area, relative to the implant, depends upon the size of the implant, and the amount of nutritive medium employed.
2. From mathematical considerations it has been possible to show that under certain conditions the frequency of occurrence of mitosis in tissue cultures is independent of the coefficient of growth rate and is equal to about 2·5%. This figure is of the same order of magnitude as the figure determined by Fischer for the frequency of mitosis in the

peripheral zone of cultures, where the conditions for growth are most favourable.

3. The conditions essential to the preparation of mitotically comparable culture groups have been determined.

Section 2.

The Proportion Between the Various Phases of Mitosis in Tissue Cultures.

The experiments to be described were performed in order to study the quantitative distribution of mitosis, amongst the various phases of division.

1. Experimental.

The tissue used was the choroid and sclerotic from 7-9 day fowl embryos grown by the hanging drop method. Small pieces of tissue were cut into fragments and each fragment was transferred to a drop of culture medium, consisting of equal parts of a mixture of fowl plasma and a saline extract of chick embryo, placed on a cover slip.

When the plasma clotted the cover slip was sealed over a hollow ground slide with paraffin wax, and the preparation incubated at 38° C. Every forty-eight hours the fragment was transferred to a fresh culture medium.

Thirty hours after the second sub-culture preparations were chosen at random, fixed, and stained.

One then counted the number of prophase, metaphase, anaphase and telophase figures contained in each preparation, but, before this was possible, it was necessary to have clearly in mind a sharp line of distinction between each phase.

In the prophase group one has counted those cells showing the various characteristic nuclear changes from the earliest recognisable up to, but not including, the arrangement of the chromosomes at the equator.

The metaphase group comprises those cells showing the various characteristic changes, from the formation of the equatorial plate up to, but not including the migration of the divided chromosomes to the poles of the spindle.

The anaphase group comprises all those cells showing the various characteristic changes from the migration of the divided chromosomes to the poles of the spindle up to but not including the appearance of constriction in the cytoplasm.

The telophase group comprises those cells showing progressive constriction of the cytoplasm; it extends up to but does not include the appearance of daughter cells. It often happens that a thin strand of cytoplasm connects the daughter cells for some time; such stages were not included in the telophase group.

In some cases one was faced with the difficulty of classifying certain "limiting forms", *i.e.*, cells which appeared to fit equally well into either of two groups; in such cases the unique method of procedure was always to classify the cell in the same way.

The classification of a small number of cells was found to be quite impossible, because, the orientation of the cell was such that the disposition of the chromosomes could not be discerned; the number of indeterminate mitoses in each preparation was recorded.

The results of counting ten different specimens are shown in Table 2. The first four columns give the percentage ratio between the number of cells in each phase and the total number of cells in mitosis.

TABLE 2.

Preparation.	Prophase. Per 100.	Metaphase. Per 100.	Anaphase. Per 100.	Telophase. Per 100.	No. of indeterminate mitoses.	No. of mitoses classified.
A	28	34	10	22	6	110
B	24	24	14	28	3	30
C	27	29	14	21	5	57
D	22	30	8	36	1	35
E	32	32	9	20	4	70
F	23	29	9	32	2	20
G	30	30	10	30	0	10
H	39	26	8	22	4	70
I	41	31	6	16	2	30
J	37	22	8	22	5	44

2. Theory.

We have already seen that, between 18 and 40 hours after the second sub-culture, the number of cells in mitosis is constant. It follows from this that the number of cells entering mitosis per unit of time is also constant, because the mean duration of mitosis is constant.[57] [58] [59] [60]

If now we represent by n_1, n_2, n_3 and n_4 the number of cells in prophase, in metaphase, in anaphase, and in telophase respectively, by t_1, t_2, t_3 and t_4 the average duration of prophase, of metaphase, of anaphase and of telophase respectively, by T_1 the mean duration of mitosis, and by N the total number of cells in mitosis, it is easy to see that we must have

$$\frac{n_1}{t_1}=\frac{n_2}{t_2}=\frac{n_3}{t_3}=\frac{n_4}{t_4}=\frac{N}{T_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

and

$$\frac{n_1}{N}=\frac{t_1}{T_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

etc.

3. Discussion.

In view of the fact that at least two sources of error are unavoidably associated with this investigation, the alterations in the ratios $\frac{n_1}{N}$, *etc.*, from one culture to another (as shown in Table 2) are not sufficiently large to indicate the existence of a real variation.

By equation 2 this means that the average time spent by the cell in the various stages of mitosis is constant.

Kemp and Juul[34] have stated that, in non-irradiated cultures, the proportion between the various phases is fairly constant, but have not given any figures in support of this statement.

4. Conclusions.

1. Under the conditions indicated the ratio between the number of cells in the various phases of mitosis and the number of cells in mitosis is fairly constant.

2. Under the conditions indicated, the ratio between the average duration of the various phases of mitosis and the average duration of mitosis is fairly constant.

Section 3.

The Mitotic Survival in Tissue Cultures Examined Immediately After Irradiation.

The objects of this investigation may be summarised as follows:

(*a*) To study the percentage survival of dividing cells in tissue cultures immediately after irradiation.

(*b*) To analyse the problem of the effect of X rays on dividing cells.

(*c*) To correlate the experimental and analytical findings, and to interpret the experimental results in terms of the conditions of irradiation and the properties of the living cell.

1. Material and Methods.

Culture Technique.—The tissue was obtained from the choroid and sclerotic of chick embryos of 8-9 days' incubation. The cultures were prepared by the hanging drop method and were grown in a medium consisting of equal parts of fowl plasma and a saline extract of embryonic chick tissue. The cover slips were measured with a micrometer screw gauge to ensure uniformity. The preparations used in these experiments were carefully selected from batches of cultures of the second subcultivation.

Radiological Technique.—A beam of approximately homogeneous radiation was used throughout this work. It is known that the probability of absorption of a quantum of energy is a function of the wave length of the radiation. It was therefore considered that the use of a monochromatic radiation was likely to enhance the possibilities of correlation and interpretation of experimental results.

Such a beam of radiation was obtained by using a tungsten target in conjunction with a filter of hafnium oxide which was well rubbed into the surface of a sheet of paper. Since the K absorption discontinuity of the filter is situated just on the hard wave length side of the K_α radiation from the target of the tube, the α radiation will be transmitted freely, the other frequencies being largely suppressed.

The tube was operated at a potential difference of 95 kilovolts, and for comparative purposes the dose of radiation administered to the cultures was approximately determined in Friedrich's "e" units.[1]

2. Experiments and Results.

A number of cultures were selected, half of which were exposed to a beam of radiation for a predetermined period, and the remaining half were fixed and stained as controls. The dose, measured in absolute units, was about "5e". During irradiation the cultures were maintained at a temperature of 38° C., and immediately after exposure the specimens were fixed and stained.

The number of dividing cells in the irradiated specimens was then counted and expressed as a percentage of that found in the controls. This ratio is referred to as the mitotic survival.

The intensity of the beam was then altered in a definite ratio by changing the current in the tube at constant potential difference, and the relative values of the intensities were determined by the ionisation method.[2] Another group of cultures was exposed to this beam, for such a period that the total dose received was equal to that given to the first group, *i.e.*, the product of relative intensity, and time was maintained constant. These were then fixed and stained together with the control cultures as before.

A series of such observations were made and one set of experimental conditions and results are summarised

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[1] The "e" unit is the quantity of radiation which will produce in 1 c.c. of air under normal conditions an amount of ionisation that, as a saturation current, will cause a change of one electrostatic unit of electricity in the measuring system.

[2] For details of this technique see "A Contribution to Biophysics", *The Med. Journ. of Australia*, Jan. 12, 1929.

in Table 3. The results are represented graphically in Fig. 3 (curve A).

TABLE 3.

Relative intensity of beam	6		3		2		1·5		1	
Duration of irradiation in minutes ..	20		40		60		80		120	
Number of cells in mitosis.	C.	I.	C.	I.	C.	I.	C.	I.	C.	I.
	43	23	56	45	53	27	37	33	59	35
	27	35	63	39	41	32	65	25	73	41
	36	32	42	50	37	29	33	29	42	27
	28	24	51	30	45	20	48	31	40	21
Totals ..	134	114	212	164	176	108	183	118	214	124
Number of sur-survivors expressed as % of controls ..	85%		77%		62%		64%		58%	

C = controls, I = irradiated.

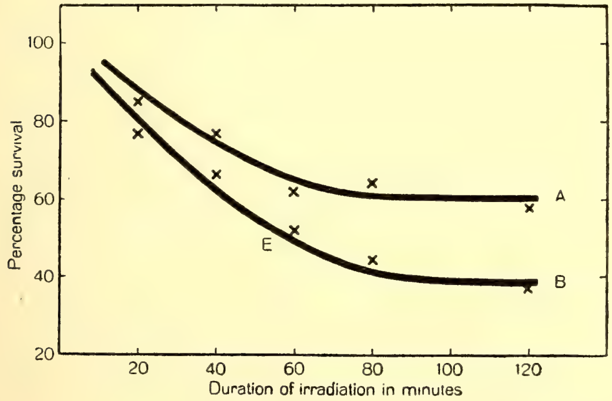

Fig. 3.

The results of similar experiments in which the dosage was increased to about "7e" are shown in Table 4, and represented graphically in Fig. 3 (curve B).

TABLE 4.

Relative intensity of beam	6		3		2		1·5		1	
Duration of irradiation in minutes ..	20		40		60		80		120	
Number of cells in mitosis.	C.	I.	C.	I.	C.	I.	C.	I.	C.	I.
	40	31	33	23	51	15	36	20	30	12
	36	28	42	31	37	21	42	21	55	22
	29	15	50	15	43	29	50	16	47	17
	38	36	39	39	28	16	51	22	23	8
Totals ..	143	110	164	108	159	81	179	79	155	59
Number of survivors expressed as % of controls ..	77%		66%		52%		44%		38%	

C = controls, I = irradiated.

Experiments were then made, in which the times of administration of a dose of "7e" units (approximately) were increased up to 4 hours. A set of observations is given in Table 5, and represented graphically in Fig. 4.

3. Discussion of Results.

From Fig. 3 we see that as the time of administration of the radiation increases from zero the number of surviving cells decreases continually. After an exposure of

TABLE 5.

Relative intensity of beam	6		3		2		1·5	
Duration of irradiation in hours ..	1		2		3		4	
Number of cells in mitosis.	C.	I.	C.	I.	C.	I.	C.	I.
	34	16	36	21	48	22	51	25
	41	21	43	15	37	19	46	19
	50	14	45	18	52	17	33	39
	37	27	67	22	29	16	39	21
Totals	162	78	190	76	166	74	169	104
Number of survivors expressed as % of controls	48%		40%		44%		61%	

C = controls, I = irradiated.

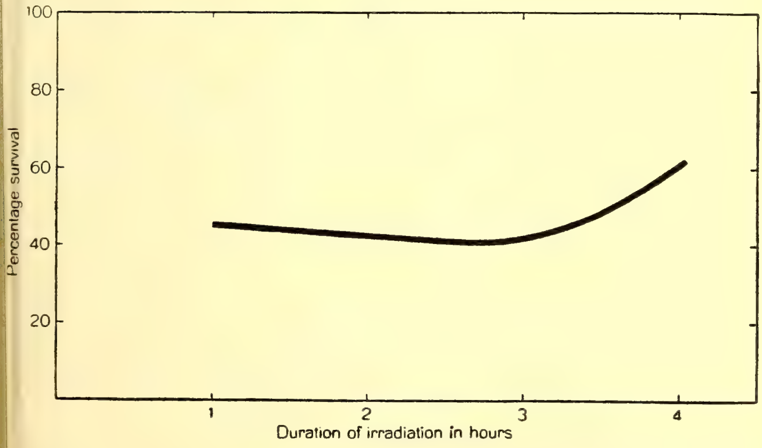

Fig. 4.

80-100 minutes the curve becomes distinctly flattened and the Bunsen-Roscoe law[1] is applicable. From Fig. 4 we see that the law again fails to apply when the time of administration of the dose is increased beyond approximately 180 minutes. At this stage the effectiveness of the dose on the culture is perceptibly reduced and the mitotic survival is in excess of that predicted by the application of the Bunsen-Roscoe law. This may be due either—

(1) To an increase in the radio-sensitivity of those cells which are distant from the dividing stage at the commencement of the experiment.

(2) To a recovery of the cells in those experiments in which the duration of irradiation was more than 180 minutes or to both.

The conditions of this experiment seem to eliminate the possibility of recovery since the cultures were fixed and stained immediately after a continuous irradiation. Results of experiments to be described subsequently afford further evidence in support of the view that the phenomenon is not due to recovery.

That irradiation with small doses produces no significant change in the average duration of the mitotic process has been shown by Spear.(82) The maximum dose administered in his experiments was sufficient to reduce the mitotic survival to about 10% after 80 minutes' incubation.

Spear's observations also mean that, under the conditions of experiment, the average duration of the mitotic process for a cell which suffered temporary inhibition is not altered.

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[1] The Bunsen-Roscoe law as applied to biological phenomena states that the quantitative effect of radiation depends on the product of the intensity of the radiation and the time of exposure.

4. Analysis of the Action of Homogeneous X Radiation on Mitosis.

The following analysis is built upon the hypotheses (1) that the decrease in the number of cells in mitosis is not due to the disintegration of cells whilst actually passing through division, but to the inhibition of some fraction of the total number of those cells which under normal circumstances would have entered division during the period of irradiation, *i.e.,* it is assumed that under the experimental conditions a cell having entered mitosis completes the process irrespective of the irradiation; (2) that the radio-sensitivity of a cell is constant throughout that portion of the inter-mitotic period considered in this analysis.

The term radio-sensitivity as used in this research may be defined as the minimum number of absorbed quanta that will just prevent a cell from entering division.

(*a*) The problem of survival in a cell group containing cells which are all in the same stage of development.

Suppose we have a number of cells all in the same given stage of development during the administration of a dose of radiation.

Let u = volume of sensitive zone or organ.[(19) (63)–(70)]

μ = coefficient of absorption of X rays in the tissue.

q = dose of radiation administered.

n = radio-sensitivity of the cells.

N = number of cells in the group.

S = number of survivors, *i.e.,* the number that enter the dividing stage.

λ = probability of absorption of one quantum of energy in the sensitive zone when unit quantity of radiation is administered.

t = time in which dose is administered.

$\alpha = \frac{dq}{dt}$ = rate of administration of radiation.

It can be readily shown that[(19) (63)–(70)]

$$S = Ne^{-\alpha\lambda t} \sum_{r=0}^{n-1} \frac{(\alpha\lambda t)^r}{\underline{|r}}$$

where $\lambda = \mu\, u$.

This result is not directly applicable to a tissue culture because, in this case, the cells under irradiation are not all equally distant (in time) from their next division.

Let us consider the case of a tissue culture by means of a diagram.

Suppose all the cells of a tissue culture to be distributed within the following diagram (Fig. 5) in such a way that B-C contains all the cells that are in the various stages of division, and let the displacement of a cell from B in the direction B-C represent the displacement of the cell in time units from the prophase stage at B where the cells are just entering division. The cells at C are dividing into daughter cells and the distance B-C is a measure of the average time spent by the cells in the dividing stage. In a similar way let the portion C-D-A-B contain all the vegetative cells and let the cell displacement in the direction B-A from B represent the displacement, in time units, of the cells from maturity.

The term "maturity" in this research is reserved for cells just about to enter the dividing stage, represented by the position of B in the above diagram.

Spear[(61)] has shown experimentally that over a certain range of time the number of cells in mitosis in a tissue culture is constant, and thus during this range of time the rate at which cells are entering mitosis must be

identical with the rate at which they are dividing into daughter cells. In a previous section I have shown that this is so from theoretical considerations. Further, these

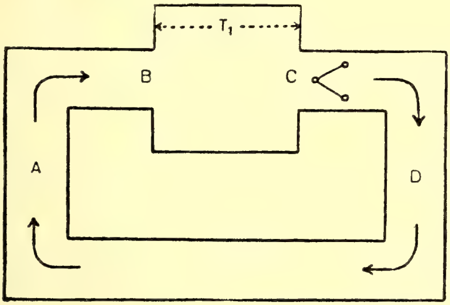

Fig. 5.

rates are fixed because the number of cells in mitosis during the equilibrium period is $\frac{dN}{dt}T_1$ where $\frac{dN}{dt}$ is the rate at which cells are entering mitosis.

(*b*) The problem of irradiation of a tissue culture followed by immediate fixation and observation.

The conditions of this problem can be represented diagrammatically by that portion of Fig. 5 reproduced in Fig. 6.

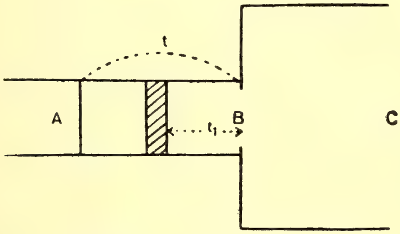

Fig. 6.

If a dose q of radiation is administered to a culture in time t, after which time the culture is fixed, stained and examined, it is seen that we are only concerned with

the effect of treatment on all those cells whose displacements from maturity (B) (Fig. 6) is less than (or equal to) t, and the individual cells in this group clearly receive doses before maturity which are proportional to their displacements from maturity. That is to say the dose received before maturity varies from cell to cell. I refer to this condition as "a non-uniform irradiation before maturity".

The number of cells in the group displaced t_1 from maturity is $\frac{dN}{dt}dt_1$, and the dose received by this group before maturity is αt_1, and hence for this group we have

$$S=\frac{dN}{dt}\left\{1+\alpha\lambda t_1+\frac{\alpha^2\lambda^2 t_1^{\,2}}{\underline{|2}}+\ldots\ldots+\frac{(\alpha\lambda t_1)^{n-1}}{\underline{|n-1}}\right\}e^{-\alpha\lambda t_1}\,dt_1$$

and the number of surviving cells in the whole group is

$$\Sigma S=\frac{dN}{dt}\left[\int_0^t e^{-\alpha\lambda t_1}dt_1+\frac{\alpha\lambda}{\underline{|1}}\int_0^t e^{-\alpha\lambda t_1}t_1\,dt_1+\;.\;\;.\;\;.\;\;.\right.$$

$$\left.+\frac{(\alpha\lambda)^{n-1}}{\underline{|n-1}}\int_0^t e^{-\alpha\lambda t_1}t_1^{\,n-1}\,dt_1\right]$$

$$=\frac{dN}{dt}\sum_{r=0}^{n-1}\frac{(\alpha\lambda)^r}{\underline{|r}}\int_0^t e^{-\alpha\lambda t}\,t^r\,dt$$

On reduction this becomes

$$\Sigma S=\frac{dN}{dt}\frac{1}{\alpha\lambda}\left[n-e^{-\alpha\lambda t}\left\{\frac{(\alpha\lambda t)^{n-1}}{\underline{|n-1}}+\frac{2(\alpha\lambda t)^{n-2}}{\underline{|n-2}}+\ldots\ldots+n\right\}\right]$$

$$=\frac{dN}{dt}\frac{t}{\lambda q}\left[n-e^{-\lambda q}\sum_{r=0}^{n-1}\frac{n-r}{\underline{|r}}\lambda^r q^r\right]$$

The percentage survival in the group is given by

$$\frac{\Sigma S}{\left(\frac{dN}{dt}\right)t}=\frac{1}{\lambda q}\left[n-e^{-\lambda q}\sum_{r=0}^{n-1}\frac{n-r}{\underline{|r}}\lambda^r q^r\right]$$

and is independent of the time in which any given dose is administered. If the cells had all remained in the same stage of development during treatment, we would have found

$$\frac{\Sigma S_1}{\left(\frac{dN}{dt}\right)t} = e^{-\lambda q} \sum_{r=0}^{n-1} \frac{\lambda^r q^r}{\lfloor r}$$

and it can be shown that

$$\frac{\Sigma S}{\Sigma S_1} = 1 + n \frac{\sum_{n}^{\infty} \frac{(\lambda q)^n}{\lfloor n+1}}{\sum_{0}^{n-1} \frac{(\lambda q)^n}{\lfloor n}}$$

and thus

$$\frac{1}{\lambda q}\left[n - e^{-\lambda q}\left\{\frac{(\lambda q)^{n-1}}{\lfloor n-1} + \frac{2(\lambda q)^{n-2}}{\lfloor n-2} + \ldots + n\right\}\right]$$
$$> \left[1 + \lambda q + \frac{\lambda^2 q^2}{\lfloor 2} + \ldots + \frac{(\lambda q)^{n-1}}{\lfloor n-1}\right] e^{-\lambda q}$$

for all values of q greater than q = o.

Two special cases must now be considered according as $t \lesseqgtr T_1$.

Case I. $t < T_1$.

During the progress of any experiment surviving cells are entering mitosis, and those cells that were in mitosis at the commencement of the irradiation are continuously passing into the daughter cell stage. These two processes are superimposed and the observed effect (E) when the specimens are fixed and stained is the algebraic sum of both these processes.

Thus when a dose q is given in time t the percentage observed survival is given by

$$E = \frac{\left(\frac{dN}{dt}\right)T_1 - \left(\frac{dN}{dt}\right)t + \Sigma S}{\left(\frac{dN}{dt}\right)T_1}$$

in which $\left(\frac{dN}{dt}\right) T_1$ is the number of dividing cells present at the commencement of the experiment, $\left(\frac{dN}{dt}\right) t$ is the number of cells that have divided into daughter cells, and ΣS is the number of surviving cells that have entered mitosis.

Thus

$$E = 1 - \frac{t}{T_1} + \frac{t}{T_1}\frac{1}{\lambda q}\left\{n - e^{-\lambda q}\sum_{r=0}^{n-1}\frac{n-r}{\underline{|r}}\lambda^r q^r\right\}$$

The factor operating on $\frac{t}{T_1}$ in the last term of the above expression is positive, independent of the time of administration of the dose and for a fixed value of the dose and radio-sensitivity it is constant (Φ), and less than unity because from the expression ΣS it is clear that

$$\Phi > o.$$

also since $\Sigma S < \left(\frac{dN}{dt}\right) t$

we have $$\Phi < 1.$$

Thus we can write $E = 1 - \frac{t}{T_1}(1 - \Phi)$

where $$o < \Phi < 1,$$

and it follows that the observed mortality[1] on the culture is greater when the time in which the dose is administered is increased.

The survival continues to decrease linearly until $t = T_1$ at which stage the value of E is given by

$$E = \Phi.$$

If we write the survival equation in the form

$$E = 1 - \frac{t}{T_1} + \frac{1}{T_1} \cdot \frac{1}{\alpha\lambda}\left\{n - e^{-\lambda q}\sum_{0}^{n-1}\frac{n-r}{\underline{|r}}\lambda^r q^r\right\}$$

[1] Percentage mortality + percentage survival = 1.

it follows that if $\alpha = \infty$
which also implies that $t = 0$
then $E = 1$
and no effect is seen in the culture. This fact is readily explained and means that, irrespective of such treatment on cells in pre-mitotic stages, no progression of the various cell groups has been possible during the administration of the dose.

Case 2. $t > T_1$.

This case is represented diagrammatically by Fig. 7.

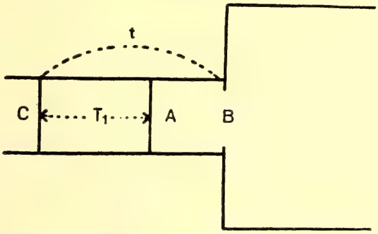

Fig. 7.

All the dividing cells present at the commencement of the experiment have become daughter cells. Since we fix and stain immediately after irradiation, it is clear that we observe the effect of the radiation on the cells in the group A-C, because the survivors from the group A-B will have become daughter cells.

Hence
$$\Sigma S = \frac{dN}{dt}\sum_{r=0}^{n-1}\frac{(\alpha\lambda)^r}{\lfloor r}\int_{t-T_1}^{t} e^{-\alpha\lambda t}t^r dt$$

and
$$E = \frac{\Sigma S}{\left(\frac{dN}{dt}\right)T_1}$$

It can be shown that E is a decreasing function of t, and thus the survival continues to decrease as the time

of administration of the dose increases from T_1 onwards.[1]

ΣS can be put in the form

$$\left(\frac{dN}{dt}\right)\frac{e^{-\lambda q}}{\alpha\lambda}\left[e^{\alpha\lambda T_1}\sum_{r=0}^{n-1}\frac{n-r}{\lfloor r}\lambda^r q^r\left(1-\frac{\alpha T_1}{q}\right)^r-\sum_{r=0}^{n-1}\frac{n-r}{\lfloor r}\lambda^r q^r\right]$$

and by expansion it can be shown that

$$\underset{\alpha\to 0}{\mathrm{Lt}}\ \Sigma S=\left(\frac{dN}{dt}\right)T_1\left[\frac{(\lambda q)^{n-1}}{\lfloor n-1}+\frac{(\lambda q)^{n-2}}{\lfloor n-2}+\ldots.+1\right]e^{-\lambda q}$$

and the individual cells of the group are now clearly receiving the equivalent of uniform irradiation before maturity.

5. Correlation and Interpretation.

There is good agreement between the theoretical and experimental results provided the duration of irradiation is less than 80 minutes (approximately). When the dose is administered over 100 minutes or more, the smaller changes in survival, predicted in the analysis, are no longer experimentally observed, being concealed within the experimental error.

The cells are now, presumably, receiving the experimental equivalent of uniform irradiation before maturity, and the Bunsen-Roscoe law becomes applicable at this point.

The linear fall of the survival curves shown in Fig. 3 is seen to occur over a period of about 40 minutes. The analysis shows that this corresponds to the time spent by the cell in the process of division. Further, this result agrees well with the average figure (34) obtained by direct observation on living cultures.[(57)(58)(59)(60)] The reduction in the gradient of the survival curve (about the

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[1] See note 1, page 152.

point E) may be ascribed to the transition between non-uniform and uniform irradiation of individual cells before maturity.

When the time of irradiation is about three hours (Fig. 4) there is an obvious divergence between experimental and analytical findings. As already indicated, this may be ascribed to a decreased radio-sensitivity of the cells whose backward displacement in time from maturity is about three hours. It is hardly possible to locate exactly the point at which the radio-sensitivity of the cells undergoes a change. The experimental results only indicate the region where the change becomes measurable by an alteration in the form of the survival curve. All we can conclude is that the results of this research are consistent with the views that—

(*a*) The radio-sensitivity of a cell changes when its displacement from maturity (backward in time) is something less than three hours.

(*b*) The radio-sensitivity of a cell is maximum and constant during the 180 minutes (approximately) preceding division.

6. Conclusions.

(1) The results of this research are consistent with the view that the decrease in the number of cells in mitosis after irradiation is due to an inhibition of some fraction of those cells that would normally have entered mitosis during the period of irradiation.

(2) Deductions from a large number of observations on stained specimens indicate that the average time spent by the cell in the process of division is about 40 minutes.

(3) The results of this research are consistent with the views that—

(*a*) The radio-sensitivity of a cell is constant and independent of its displacement from maturity provided that the displacement is less than about three hours.

(*b*) The radio-sensitivity of a cell undergoes a change when its displacement from maturity is greater than about 180 minutes.

(4) When cultures are fixed immediately after irradiation the Bunsen-Roscoe law is applicable to the process of inhibition of mitosis provided that—

(*a*) The time of irradiation is in excess of a period of about 100 minutes. In accordance with our interpretation of experimental results this period of 100 minutes can be identified with the period required to produce the experimental equivalent of a "uniform irradiation" before maturity.

(*b*) The duration of irradiation is less than about 180 minutes. In accordance with our interpretation of experimental results, this period of 180 minutes can be identified with the period required for cells, in the region of reduced radio-sensitivity at the commencement of irradiation, to enter mitosis.

Section 4.

The Mitotic Survival in Tissue Cultures Incubated for a Period of Eighty Minutes After Irradiation.

The objects of this investigation may be classified as follows:

(*a*) To study the percentage survival of dividing cells in irradiated tissue cultures, incubated for 80 minutes before fixation.

(*b*) To analyse the problem of mitotic survival in these irradiated tissue cultures.

(*c*) To correlate the experimental and analytical findings.

1. Experiments and Results.

The general cultural and radiological techniques were the same as already described in Section 3.

A number of cultures were selected, half of which were irradiated, and the other half were fixed and stained as controls. During the irradiation the cultures were maintained at 38° C., and after exposure were returned to the incubator for a period of 80 minutes before being fixed and stained. The mitotic survival was determined as before, and this gave a measure of the effect of the treatment (irradiation plus incubation) on mitosis.

The tube current and potential difference were maintained at a constant value, and a series of cultures were irradiated for various lengths of time. The intensity of the beam in absolute units was about "5e" per 15 minutes. The relation between mitotic survival and duration of irradiation was thus determined and the result plotted as a graph.

The intensity was then altered in a simple ratio (2:1) by changing the current in the tube, at constant potential difference and another survival curve was determined. This was repeated with other intensities until a series of curves were obtained.

As before, the relative values of the intensities (1:2:4:8) were measured by the ionisation method.

Table 6 shows the results of a series of observations, and these are represented graphically in Fig. 8. In this

figure a dotted line is also drawn, indicating the mitotic survival for constant dosage.

TABLE 6.

Intensity—1.

Duration of irradiation in minutes ..	90		120		160		200	
Number of cells in mitosis.	C.	I.	C.	I.	C.	I.	C.	I.
	36	28	36	31	40	21	41	26
	51	40	51	28	31	35	59	40
	32	34	32	25	63	26	63	38
	40	34	40	42	35	31	48	27
Totals	159	136	159	126	169	113	211	131
Number of survivors expressed as % of controls	86%		80%		67%		62%	

Intensity—2.

Duration of irradiation in minutes ..	40		80		120		160	
Number of cells in mitosis.	C.	I.	C.	I.	C.	I.	C.	I.
	43	50	47	23	51	9	56	6
	55	36	33	11	47	16	48	18
	33	27	46	26	62	23	37	13
	52	54	42	9	38	9	29	7
Totals	183	167	168	69	198	57	170	44
Number of survivors expressed as % of controls	91%		41%		29%		26%	

Intensity—4.

Duration of irradiation in minutes ..	20		30		40		55	
Number of cells in mitosis.	C.	I.	C.	I.	C.	I.	C.	I.
	41	35	51	29	38	17	38	8
	52	41	42	32	31	13	52	20
	50	33	50	23	45	15	39	15
	39	41	48	34	36	17	50	16
Totals	182	150	191	118	150	62	179	59
Number of survivors expressed as % of controls	82%		62%		41%		33%	

Intensity—8 ("5e" per 15 minutes).

Duration of irradiation in minutes ..	10		15		20		30		40	
Number of cells in mitosis.	C.	I.	C.	I.	C.	I.	C.	I.	C.	I.
	47	32	36	21	41	20	43	14	41	8
	40	36	65	29	36	11	41	10	39	3
	38	25	29	32	42	15	51	8	42	6
	42	43	36	18	39	16	40	19	49	5
Totals ..	167	136	166	100	158	62	175	51	171	22
Number of survivors expressed as % of controls ..	82%		60%		39%		29%		13%	

C = controls, I = irradiated.

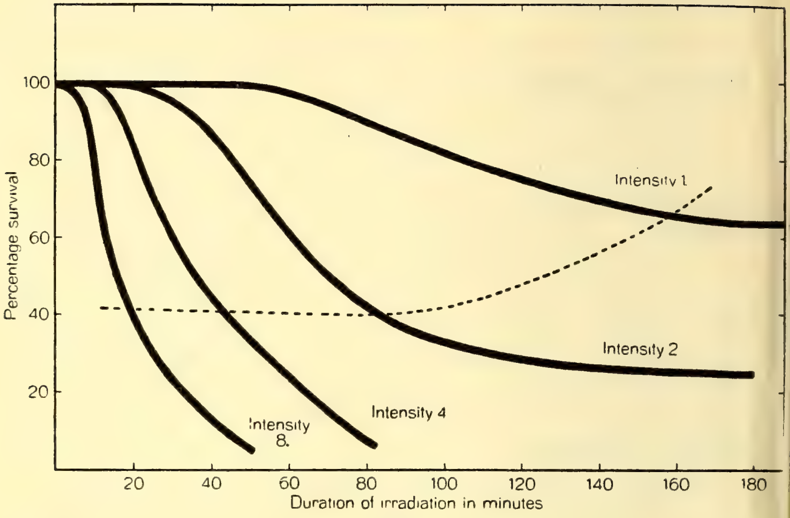

Fig. 8.

2. Discussion.

It is apparent from Fig. 8 that, for exposure times up to about 100 minutes, the Bunsen-Roscoe law is applicable to the process by which cells are inhibited from entering mitosis by X radiation. As the time of exposure is further increased the survival curves become flattened and the Bunsen-Roscoe law is no longer applicable, the actual survival being greater than that calculated by the application of the law. This may conceivably be explained either by—

(1) an increase in the radio-sensitivity of those cells which are distant from the dividing stage at the commencement of irradiation, or

(2) a recovery of cells during the period of incubation, or by a combination of both processes.

Evidence has been produced in a previous section to show that an increase in radio-sensitivity is the more

likely explanation. This is further confirmed by later experimental work.

3. Analysis.

If we analyse this problem as in the previous section, the conditions can be represented by that portion of Fig. 5 reproduced in Fig. 9 where

t_1 = the time spent in the administration of the dose of radiation.

t_2 = the duration of incubation subsequent to irradiation.

T_1 = the average time spent by the cell in the process of division.

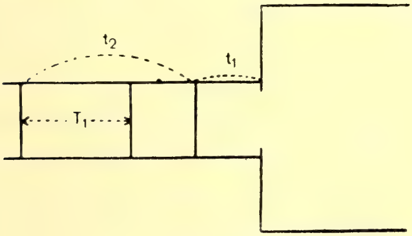

Fig. 9.

we see that

(1) at the termination of treatment (irradiation and incubation) all the dividing cells present at the commencement of the experiment have become daughter cells because $t_1 + t_2$ is greater than T_1;

(2) at the termination of treatment all the surviving cells from the group whose boundaries have co-ordinates $0, (t_2 + t_1 - T_1)$ have become daughter cells;

(3) the co-ordinates of the boundaries of the cell group that comes under our observation when we fix and stain are $(t_1 + t_2)$, $(t_1 + t_2 - T_1)$;

(4) the individuals of this group have all received "uniform irradiation" before maturity because the co-

ordinate of each boundary is not less than the time spent in the administration of the radiation;

(5) the mitotic survival will, under these conditions of "uniform irradiation" before maturity, depend only on the dose of radiation administered, provided that the radio-sensitivity of a cell is independent of its displacement from maturity. The Bunsen-Roscoe law will be applicable and the time of administration of the dose will have no significance.

4. Correlation and Interpretation.

When the time of irradiation plus incubation is less than 180 minutes (approximately) there is a good agreement between the experimental and the theoretical results, *i.e.,* the deductions from our hypotheses have been experimentally realised.

When the time of irradiation plus incubation is greater than 180 minutes approximately there is no longer an agreement. A measurable increase in the mitotic survival occurs in the cell group (180), ($180 - T_1$), and this can be ascribed to the presence of surviving cells from a region of reduced radio-sensitivity. This does not necessarily mean that the radio-sensitivity of a cell changes abruptly when its backward displacement in time from maturity is about 180 minutes. All we can conclude is that the experimental results are consistent with the view that there is a change in the radio-sensitivity of a cell near that point.

It may be noted that from the survival curves in Fig. 8 we could construct curves showing:

(*a*) The effect of increased dosage on pre-mitotic cell groups of given displacement from maturity.

(*b*) The effect of a constant dosage on cell groups progressively displaced from maturity.

In the region represented by (t_2+t_1) (Fig. 9) the radio-sensitivity of a cell is independent of its backward displacement from B, provided that t_2+t_1 is less than 180 minutes (approximately). We can now arrive at an estimate of the radio-sensitivity of a cell in this region in terms of quanta.

The survival curves in Fig. 8 represent the result of "uniform irradiation" of cells in pre-mitotic stages and the survival equation (*vide* Section 3) is of the form—

$$\frac{S}{N}=\left\{1+\lambda q+\frac{\lambda^2q^2}{\underline{|2}}+\ldots+\frac{(\lambda q)^{n-1}}{\underline{|n-1}}\right\}e^{-\lambda q}$$

It can be shown that at the point of inflexion of the survival curves in Fig. 8 we have

$$\lambda q = n-1$$

and at this point

$$q\frac{d}{dq}\left(\frac{S}{N}\right)=\frac{-e^{-(n-1)}(n-1)^{n-1}}{\underline{|n-2}}$$
$$=-\Phi(n).$$

This function has been tabulated, and from the survival curves it is possible to get some idea of the value $q\frac{d}{dq}\left(\frac{S}{N}\right)$ at the point of inflexion, but this point cannot be located very accurately. The approximate value is 0·8, and thus n is approximately 6. Hence it appears that about 6 quanta are required to be absorbed to prevent the cell from entering mitosis.

5. Conclusions.

(1) The results of this research are consistent with the view that the reduction in the number of cells in mitosis after irradiation is due to an inhibition of some fraction of those cells which normally would have entered mitosis during the period of irradiation.

(2) Provided that the duration of irradiation plus the subsequent incubation is less than 180 minutes (approximately), the Bunsen-Roscoe law is applicable to the process of mitotic inhibition.

(3) The results of this research are consistent with the views that—

- (*a*) The radio-sensitivity of a cell is constant and independent of its displacement from maturity, provided that the displacement is less than about 180 minutes.
- (*b*) The radio-sensitivity of a cell decreases when its displacement from maturity is greater than about 180 minutes.

(4) When the displacement of a cell from maturity is less than about 180 minutes, 6 absorbed quanta (approximately) are required to prevent the cell from entering division.

Section 5.

The Mitotic Survival in Tissue Cultures when the Time of Irradiation Plus Subsequent Incubation is Maintained Constant.

The objects of this investigation may be classified as follows:

- (*a*) To study the percentage survival of dividing cells in tissue cultures when the duration of irradiation plus subsequent incubation is maintained constant.
- (*b*) To analyse the problem of mitotic survival in these irradiated tissue cultures.
- (*c*) To correlate the experimental and theoretical findings.

1. Experiments and Results.

The general radiological and cultural techniques were the same as described in Section 3.

A batch of cultures was irradiated for a period of five minutes, and the dose administered in absolute units was about "5e". At the termination of irradiation the cultures were returned to the incubator for 35 minutes; they were then fixed and stained, together with the controls.

The intensity of the beam was then reduced to $\frac{1}{8}$th of its previous value and a second batch of cultures was irradiated for a period of 40 minutes, when they were fixed and stained. Each group of cultures thus received the same dose.

The experimental conditions, and the number of mitotic figures in the irradiated and control cultures are shown in Table 7.

TABLE 7.

Relative intensity of beam ..	8		1	
Duration of irradiation in minutes ..	5		40	
Duration of incubation in minutes ..	35		0	
Number of cells in mitosis	C.	I.	C.	I.
	33	15	37	23
	45	21	29	35
	28	19	45	17
	40	8	52	23
Totals	146	63	163	98
Number of survivors expressed as % of controls	43%		60%	

C = controls, I = irradiated.

Two more batches of cultures were then similarly irradiated, the beam intensities being in the ratio 3:2, and the period of incubation was adjusted accordingly. The experimental conditions and mitotic counts are recorded in Table 8.

TABLE 8.

Relative intensity of beam ..	3		2	
Duration of irradiation in hours ..	2		3	
Duration of incubation in hours ..	1		0	
Number of cells in mitosis ..	C.	I.	C.	I.
	25	10	38	23
	34	32	42	12
	27	26	36	15
	56	16	21	28
Totals	142	84	137	78
Number of survivors expressed as % of controls	59%		57%	

C = controls, I = irradiated.

2. Discussion.

From Table 7 it is seen that a reduction in the time of administration (with a corresponding increase in intensity) was accompanied by a reduction in the mitotic survival. From Table 8 it is seen that a reduction in

the time of administration of the dose was not accompanied by a significant reduction in the mitotic survival.

3. Analysis.

If we analyse this problem as in Section 3, three cases arise for consideration according as $t_1 + t_2 \lesseqqgtr T_1$, where

t_1 = the time of administration of a given dose of radiation,

t_2 = the duration of incubation subsequent to irradiation.

Case 1. $t_1 + t_2 < T_1$.

These conditions are represented diagrammatically by that portion of Fig. 5 reproduced in Fig. 10.

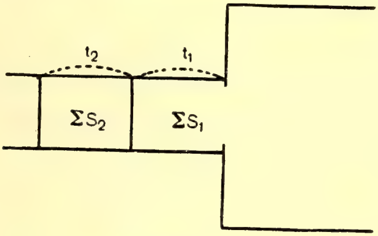

Fig. 10.

If the number of surviving cells in the group t_1 is ΣS_1 and the number of surviving cells in the group t_2 is ΣS_2 we have

$$\Sigma S_1 = \left(\frac{dN}{dt}\right)\frac{t_1}{\lambda q}\left\{n - e^{-\lambda q}\sum_{r=0}^{n-1}\frac{n-r}{\lfloor r}\lambda^r q^r\right\}$$

$$\Sigma S_2 = \left(\frac{dN}{dt}\right) t_2 e^{-\lambda q}\sum_{r=0}^{n-1}\frac{\lambda^r q^r}{\lfloor r}$$

To find the effect of altering t_1 we determine $\frac{d}{dt_1}[\Sigma S_1 + \Sigma S_2]$ subject to the condition

$$t_1 + t_2 = \text{constant}$$

We find that

$$\frac{d}{dt_1}[\Sigma S_1+\Sigma S_2]=\frac{dN}{dt}\left\{\frac{1}{\lambda q}\left[n-e^{-\lambda q}\sum_{r=0}^{n-1}\frac{n-r}{\underline{|r}}\lambda^r q^r\right]-e^{-\lambda q}\sum_{r=0}^{n-1}\frac{\lambda^r q^r}{\underline{|r}}\right\}$$

which is clearly positive.

Thus as t_1 increases the survival increases and the mortality decreases.

Thus the mortality sustained in a group of cells that are approaching a state of maturity is increased by reducing the time in which a given dose is administered.

If we write $t_1 + t_2 = t_3 =$ constant, we have

$$\underset{t_1\to 0}{\mathrm{Lt}}[\Sigma S_1+\Sigma S_2]=\left(\frac{dN}{dt}\right)t_3 e^{-\lambda q}\sum_{r=0}^{n-1}\frac{\lambda^r q^r}{\underline{|r}}$$

and

$$\underset{t_2\to 0}{\mathrm{Lt}}[\Sigma S_1+\Sigma S_2]=\left(\frac{dN}{dt}\right)\frac{t_3}{\lambda q}\left[n-e^{-\lambda q}\sum_{r=0}^{n-1}\frac{n-r}{\underline{|r}}\lambda^r q^r\right]$$

Hence $\Sigma S_1 + \Sigma S_2$ increases in value from

$$\left(\frac{dN}{dt}\right)t_3 e^{-\lambda q}\sum_{r=0}^{n-1}\frac{\lambda^r q^r}{\underline{|r}}$$

to the value

$$\left(\frac{dN}{dt}\right)t_3\cdot\frac{1}{\lambda q}\left[n-e^{-\lambda q}\sum_{r=0}^{n-1}\frac{n-r}{\underline{|r}}\lambda^r q^r\right]$$

as the time of administration of the treatment increases from zero to t_3. The "observed effect" on the culture in this case takes the form

$$E=\frac{\left(\frac{dN}{dt}\right)T_1-\left(\frac{dN}{dt}\right)(t_1+t_2)+\Sigma S_1+\Sigma S_2}{\left(\frac{dN}{dt}\right)T_1}$$

Now since

$$\frac{dE}{dt_1}=\frac{d}{dt_1}[\Sigma S_1+\Sigma S_2]$$

the observed mortality is clearly increased by reducing the time occupied by the irradiation.

Case 2. $t_1 + t_2 > T_1$.

These conditions are represented diagrammatically by Fig. 11.

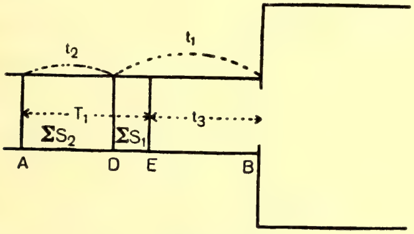

Fig. 11.

Let $t_1 + t_2 - t_3 = T_1$.

Then if the survivors from the group A-D (Fig. 11) are ΣS_2 and those from the group D-E are ΣS_1 we have

$$\Sigma S_2 = \left(\frac{dN}{dt}\right) t_2 e^{-\lambda q} \sum_{r=0}^{n-1} \frac{\lambda^r q^r}{\lfloor r} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\Sigma S_1 = \left(\frac{dN}{dt}\right) \frac{1}{\alpha\lambda} \left\{ e^{-\alpha\lambda t_3} \sum_{r=0}^{n-1} \frac{n-r}{\lfloor r} (\alpha\lambda t_3)^r - e^{-\alpha\lambda t_1} \sum_{r=0}^{n-1} \frac{n-r}{\lfloor r} (\alpha\lambda t_1)^r \right\}$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In this case it is clear that the observed effect (E) on the culture depends only on $\Sigma S_1 + \Sigma S_2$ and in determining the variation of $\Sigma S_1 + \Sigma S_2$ with t_1 we note that the variations in α and t_1 are such that

$$\alpha t_1 = q = \text{constant}.$$

By an application of the Theorem of Mean Value it can be shown that the survival decreases as t_2 increases, and that it increases as t_1 increases.[1]

[1] See note 2, page 152.

When $t_2 = 0$, $\Sigma S_2 = 0$ and the survival is given by equation (2), and when $t_2 = T_1$, $\Sigma S_1 = 0$, and the survival is given by

$$\Sigma S_2 = \left(\frac{dN}{dt}\right) T_1 e^{-\lambda q} \sum_{r=0}^{n-1} \frac{\lambda^r q^r}{\underline{|r}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The survival cannot be further reduced by further reduction in t_1. Thus, if the time spent in the administration of irradiation plus incubation is constant and exceeds the average time spent by the cell in the dividing stage (T_1) by a time t_3 then we see that if the time spent in the administration of the dose is less than t_3 the survival has a minimum value given by equation (3).

This value is maintained until t_1 just exceeds t_3 and from this instant the survival steadily increases up to the value given by equation (2) corresponding to time

$$t_2 = 0$$

ΣS_1 can be put in the form

$$\Sigma S_1 = \left(\frac{dN}{dt}\right) \frac{e^{-\lambda q}}{\alpha\lambda} \left[e^{\alpha\lambda T_1} \sum_{r=0}^{n-1} \frac{n-r}{\underline{|r}} \lambda^r (q-\alpha T_1)^r - \sum_{r=0}^{n-1} \frac{n-r}{\underline{|r}} \lambda^r q^r \right]$$

and it can be shown, when the dose is given infinitely slowly, that ΣS_1 and ΣS_2 become identical. This means that the cell group under consideration must be infinitely distant from the dividing stage.

Case 3. $t_1 + t_2 = T_1$.

These conditions are represented diagrammatically by Fig. 12.

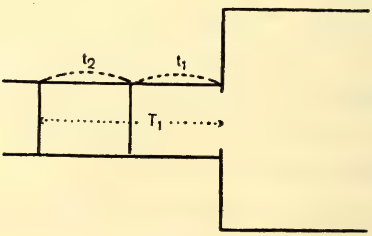

Fig. 12.

All the dividing cells present at the commencement of the experiment have passed to the daughter cell stage, and the observed effect (E) depends only on $\Sigma S_1 + \Sigma S_2$. As before, $\Sigma S_1 + \Sigma S_2$ increases from the value

$$\Sigma S_1 = \left(\frac{dN}{dt}\right) T_1 e^{-\lambda q} \sum_{r=0}^{n-1} \frac{\lambda^r q^r}{\underline{|r}}$$

corresponding to the survival when the dose is given in an infinitely short time $t_1 = 0$ up to the value

$$\Sigma S_2 = \left(\frac{dN}{dt}\right) \frac{T_1}{\lambda q} \left\{ n - e^{-\lambda q} \sum_{r=0}^{n-1} \frac{n-r}{\underline{|r}} \lambda^r q^r \right\}$$

corresponding to the administration of the dose in time T_1.

4. Correlation and Interpretation.

Over the range of cell displacements considered in this section, there is a good agreement between the theoretical and experimental results, *i.e.*, the deductions from our hypotheses have been experimentally realised.

The analysis shows that when the time of irradiation plus incubation is 40 minutes, the difference in mitotic survival (43% and 60% seen in Table 6) may be ascribed to the difference in the dosage received by the individual cells before maturity.

In the case of cultures irradiated for five minutes and incubated for 35 minutes the fixed mitotic cells have apparently received an irradiation before maturity which was approximately "uniform".

In the case of cultures irradiated 40 minutes and incubated 0 minutes the fixed mitotic cells have presumably received an irradiation before maturity which was not uniform.

When the time of irradiation plus incubation is three hours the difference in mitotic survival (59% and 57%

seen in Table 7) is not experimentally significant. This is because the difference predicted for this case by the analysis is concealed within the experimental error (10%).

5. Conclusions.

(1) The results of this research are consistent with the view that the reduction in the number of cells in mitosis is due to an inhibition of some fraction of those cells which normally would have entered mitosis during the period of irradiation.

(2) The results of this research are consistent with the view that the radio-sensitivity of a cell, whose backward displacement in time from maturity is less than 180 minutes approximately, is constant and independent of the displacement.

Section 6.

The Mitotic Survival in Tissue Cultures Incubated for Various Periods Subsequent to Irradiation.

Experiments have been described in previous sections concerning the effects of X radiation on mitosis *in vitro* when cultures were examined either immediately after irradiation or after a short period of incubation subsequent to irradiation. It is now proposed to consider the changes which occur in cultures which are irradiated and then incubated for prolonged periods before fixation.

Kemp and Juul,[34] employing a beam of heterogeneous X radiation, found that the mitotic count in tissue cultures fell subsequently to irradiation and reached a minimum value in about one hour. On further incubation, however, the mitotic count increased and, provided the dose had not been too large, reached the normal in

about three hours. A slight rise in the mitotic count above normal was noticed but no significance was attached by these workers to this observation. Previous to this, Canti and Spear[43] had exposed tissue cultures to radium and showed that after a short irradiation the initial fall in mitosis was followed by a definite rise above normal. The mitosis was a maximum about four hours after irradiation and the increase compensated almost exactly for the previous diminution in mitosis.

The objects of the present investigation may be summarised as follows:

(*a*) To study the effect of approximately homogeneous X radiation on mitosis in tissue cultures incubated for various periods subsequent to irradiation.

(*b*) To analyse the problem of mitotic survival in these irradiated cultures.

(*c*) To correlate the experimental and theoretical results.

1. Experiments and results.

The general radiological and cultural techniques were the same as described in Section 3.

A batch of cultures was irradiated for a period of ten minutes, and the dose administered, in absolute units, was about "5e". They were then fixed and stained together with the controls. Further batches of cultures were then irradiated and returned to the incubator for periods of 20, 40, 60 and 80 minutes before fixation.

Table 9 summarises the conditions of the experiment and the number of mitotic figures in the irradiated and control cultures. These results are represented graphically in Fig. 13.

TABLE 9.

Period of incubation in minutes ..	0		20		40		60		80	
Number of cells in mitosis.	C.	I.	C.	I.	C.	I.	C.	I.	C.	I.
	35	31	35	23	35	18	35	27	35	24
	41	29	41	32	41	23	41	31	41	18
	37	35	37	19	37	15	37	19	37	31
	29	41	29	36	29	35	29	30	29	22
Totals ..	142	136	142	110	142	91	142	90	142	95
Number of survivors expressed as % of controls ..	96%		78%		64%		63%		67%	

C = controls, I = irradiated.

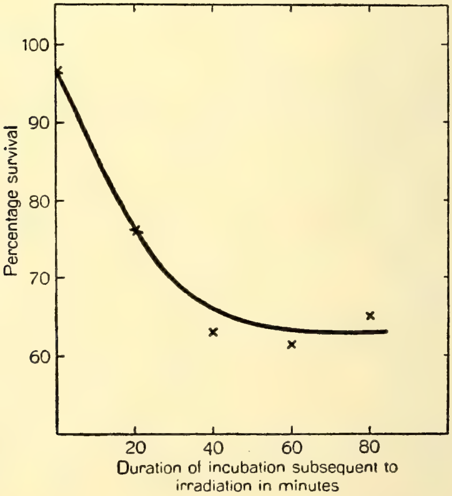

Fig. 13.

In a further series of similar experiments, the periods of incubation subsequent to irradiation were increased up to six hours. The results are summarised in Table 10, and are represented graphically in Fig. 14.

TABLE 10.

Period of incubation ..	60 mins.		80 mins.		4 hrs.		6 hrs.	
	C.	I.	C.	I.	C.	I.	C.	I.
Number of cells in mitosis	26	21	36	32	28	30	33	26
	31	13	41	24	37	43	51	41
	42	23	28	18	22	28	26	33
	55	33	52	12	45	61	37	50
Totals	154	90	157	86	132	162	147	150
Number of survivors expressed as % of controls	58%		55%		123%		102%	

C = controls, I = irradiated.

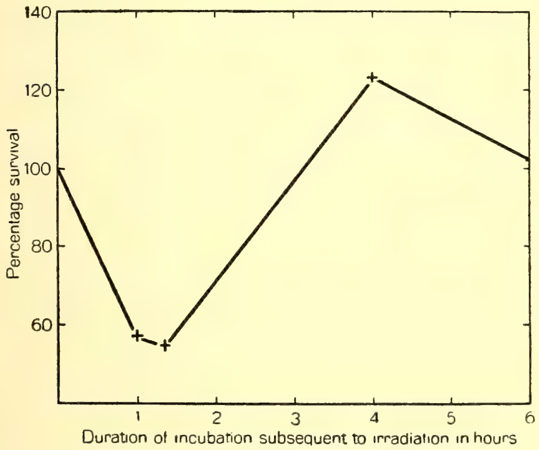

Fig. 14.

2. Discussion.

From Fig. 13 it is seen that the gradient of the curve representing mitotic survival falls continuously for a period of about forty minutes; it then becomes rapidly reduced to zero.

From Fig. 14 it is seen that an increase in the mitotic survival commences when the incubation period is about 80 minutes. This observation is in good agreement with those of Canti and Spear[43] and Kemp and Juul.[34]

The process by which this return of mitosis takes place is undoubtedly due to a recovery of cells that were temporarily inhibited from entering mitosis. After four hours' incubation, however, the survival definitely rises above normal. Canti and Spear[43] state three possible explanations.

(1) The number of cells entering mitosis per unit of time is increased.

(2) The time occupied for the process of mitosis to take place is increased.

(3) A combination of both processes.

In a later publication, Spear[82] was able to state that irradiation produces no significant change in the average duration of the mitotic process and therefore advanced the explanation that the increase in the survival above normal is due to the fact that the number of cells entering mitosis per unit of time is increased.

3. Analysis.

If we analyse this problem as in Section 3, two cases arise for consideration according as to whether

$$t_1 + t_2 \lesseqgtr T_1$$

where t_1 = the time of exposure to the radiation

t_2 = the duration of incubation subsequent to irradiation.

Case 1. $t_1 + t_2 < T_1$.

The conditions of this problem can be represented diagrammatically by that portion of Fig. 5 reproduced in Fig. 15.

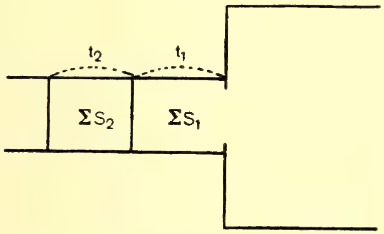

Fig. 15.

If ΣS_1 represents the number of surviving cells from the cell group t_1, and ΣS_2 represents the number of surviving cells from the group t_2 we have.

$$\Sigma S_1 = \left(\frac{dN}{dt}\right)\frac{t_1}{\lambda q}\left\{n - e^{-\lambda q}\sum_{r=0}^{n-1}\frac{n-r}{\underline{|r}}\lambda^r q^r\right\}$$

$$\Sigma S_2 = \left(\frac{dN}{dt}\right) t_2 e^{-\lambda q}\sum_{r=0}^{n-1}\frac{\lambda^r q^r}{\underline{|r}}$$

Since q is constant it follows that the observed effect on the culture is given by

$$E = \frac{\left(\frac{dN}{dt}\right)T_1 - \left(\frac{dN}{dt}\right)(t_1+t_2) + \Sigma S_1 + \Sigma S_2}{\left(\frac{dN}{dt}\right)T_1}$$

$$= 1 - \frac{t_1}{T_1}(1-\Phi_1) - \frac{t_2}{T_1}(1-\Phi_2)$$

where Φ_1 and Φ_2 are each constant and < 1.

It can now be seen that as incubation continues E decreases linearly until

$$t_1 + t_2 = T_1$$

and at this stage all the dividing cells present at the

commencement of the experiment have become daughter cells and the value of E is now given by

$$E = \frac{t_1}{T_1}\Phi_1 + \frac{t_2}{T_1}\Phi_2$$

Case 2. $t_1 + t_2 > T_1$.

The conditions in this case can be represented diagrammatically by Fig. 16.

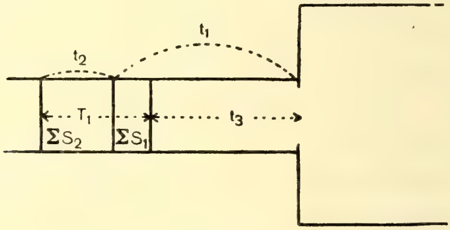

Fig. 16.

The value of t_2 has now increased beyond that given by

$$t_2 = T_1 - t_1$$

and E is given by the equation

$$E = \frac{\Sigma S_1 + \Sigma S_2}{\frac{dN}{dt} \cdot T_1}$$

We have

$$\Sigma S_1 = \left(\frac{dN}{dt}\right)\left\{\sum_{r=0}^{n-1}\frac{(\alpha\lambda)^r}{\underline{|r}}\int_0^{t_1} e^{-\alpha\lambda t}t^r dt - \sum_{r=0}^{n-1}\frac{(\alpha\lambda)^r}{\underline{|r}}\int_0^{t_3} e^{-\alpha\lambda t}t^r dt\right\}$$

$$\Sigma S_2 = \left(\frac{dN}{dt}\right) t_2 e^{-\lambda q}\sum_{r=0}^{n-1}\frac{\lambda^r q^r}{\underline{|r}}$$

where $t_3 = t_1 + t_2 - T_1$.

It can now be shown that

$$\frac{d}{dt_3}[\Sigma S_1 + \Sigma S_2] \text{ is negative}$$

but the decrease in E with incubation is no longer linear

and $\Sigma S_1 + \Sigma S_2$ attains a minimum value given by the equation

$$\Sigma S_2 = \left(\frac{dN}{dt}\right) T_1 e^{-\lambda q} \sum_{r=0}^{n-1} \frac{\lambda^r q^r}{\lfloor r}$$

when $t_2 = T_1$.

At this stage all the cells in the group under consideration have received "uniform irradiation" before maturity and there will be no further change in the observed effect on the culture unless (1) the radio-sensitivity of a cell is a function of its displacement from maturity, (2) a recovery of cells takes place.

4. Correlation and interpretation.

There is good agreement between the theoretical and experimental results provided the period of incubation subsequent to irradiation is not more than about 80 minutes. After this period cells that were temporarily inhibited from entering mitosis by the X radiation begin to recover and the mitotic count steadily increases until it reaches normal. A complete recovery, however, could only bring the mitotic count of the irradiated cultures up to that of the controls.

In previous work I have shown that there was a measurable change in the mitotic survival in irradiated tissue cultures. This was apparently due to a decrease in the radio-sensitivity of those cells whose displacement (backward in time units) from maturity was greater than 180 minutes (approximately).

From the work of Kemp and Juul and Canti and Spear it is evident that the ability of a culture to recover is a function of the dose of radiation administered.

The dose administered in the experiments described in this section temporarily reduced the mitotic survival

to about 50% of that seen in the controls, when the specimens were examined after 80 minutes' incubation. We may reasonably assume that cell recovery was complete or almost complete in those cultures which were incubated for three hours or more subsequent to irradiation.

The increase is the mitotic survival above normal observed in these experiments, therefore, appears to be due to a complete or almost complete recovery of temporarily inhibited cells superimposed on an increased survival (due to decreased radio-sensitivity) in those cell groups which were displaced (backwards in time units) from maturity to the extent of about 180 minutes at the commencement of the irradiation. The conditions of this problem can be represented diagrammatically by the portion of Fig. 5 reproduced in Fig. 17.

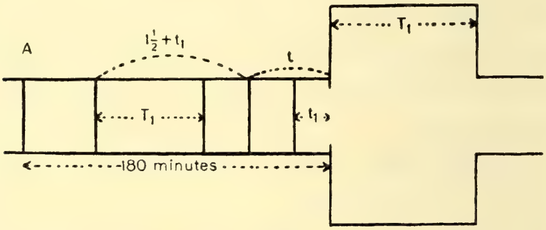

Fig. 17.

If a small dose of radiation is administered to a culture in time t, and the culture is then incubated for a period of $1\frac{1}{2} + t_1$ hours, it is clear that the "inhibited" cells from the group whose co-ordinates are 0 and t_1 are now superimposed on the survivors from the group whose co-ordinates are

$$(1\tfrac{1}{2} + t + t_1),\ (1\tfrac{1}{2} + t + t_1 - T_1).$$

As t_1 is increased the position of the cell group $(1\frac{1}{2} + t + t_1)$, $(1\frac{1}{2} + t + t_1 - T_1)$ progresses towards A,

the point at which the radio-sensitivity becomes reduced and ultimately passes beyond this point. Now when $t_1 = 3$ hours the co-ordinates of the cell group in which recovery is occurring are $3\ (3 - T_1)$, and all the cells in this group receive "uniform irradiation" and consequently the inhibition produced is maximum. This inhibition is now superimposed on a cell group whose co-ordinates are

$$(4\tfrac{1}{2} + t),\ (4\tfrac{1}{2} + t - T_1)$$

and which is situated in the region of reduced radio-sensitivity. Hence the maximum inhibition becomes a maximum recovery and this is superimposed on an increased survival due to the reduced radio-sensitivity, and it would appear that the stimulation assumes a maximum value when the duration of incubation subsequent to treatment is equal to about $4\frac{1}{2}$ hours. At this point the maximum inhibition is superimposed on the survival in a cell group displaced to the maximum extent into the region of reduced radio-sensitivity. This conclusion is in good agreement with the result of my own experiments and with the observations of Canti and Spear.

Theoretically this stimulation should persist if the radio-sensitivity continues to decrease with increasing displacement from maturity and thus such a treatment as described would have the effect of permanently stimulating a culture.

5. Conclusions.

The results of the researches described in this and in the three previous sections indicate that:

(1) The radio-sensitivity of a cell is a function of its displacement from maturity.

(2) The radio-sensitivity of a cell is constant and independent of its displacement from maturity provided that the displacement is less than about 180 minutes.

(3) The radio-sensitivity of a cell decreases when its displacement from maturity is greater than about 180 minutes.

(4) The reduction in the number of dividing cells in an irradiated tissue culture is due to an inhibition of some fraction of those cells which normally would have entered mitosis during the process of irradiation.

(5) The temporary increase in the mitotic count of an irradiated culture after four hours' incubation is due to the superimposition of a complete or almost complete recovery of temporarily inhibited cells on an increased survival (due to decreased radio-sensitivity) in those cell groups displaced from maturity to the extent of about three hours at the commencement of experiment.

Section 7.

The Diminution in the Number of the Various Phases of Mitosis in Irradiated Tissue Cultures.

An experimental study relating to the disappearance of the mitotic phases from irradiated tissue cultes has been made by Kemp and Juul.[34] I have made an analysis of this problem, built on the hypothesis that the disappearance of mitoses from irradiated tissue cultures is due to inhibition, and not due to disintegration. The similarity between the analytical and experimental results is very striking.

1. Analysis.

We have already shown that, under certain conditions, the number of cells entering mitosis per unit of time in normal tissue cultures is constant $\left(\frac{dN}{dt}\right)$.

If now we let

t_1 = the average duration of prophase

t_2 = the average duration of metaphase

t_3 = the average duration of anaphase

t_4 = the average duration of telophase

T_1 = the average duration of mitosis

we may immediately formulate the following results:

$$T_1 = \sum_{r=1}^{4} t_r$$

$$n_1 = \left(\frac{dN}{dt}\right) t_1$$

$$n_2 = \left(\frac{dN}{dt}\right) t_2$$

etc.,

and

$$\sum_{r=1}^{4} n_r = \left(\frac{dN}{dt}\right) T_1$$

where n_1, n_2, n_3 and n_4 represent the number of cells in prophase, in metaphase, in anaphase and in telophase respectively.

If the diminution in the number of mitoses in an irradiated tissue culture is due to the inhibition of a proportion of those cells which normally would have entered mitosis during the period corresponding to the irradiation, then, after the administration of a dose, just sufficient to ensure the disappearance of all the phases of mitosis, the disappearance of the various phases will

be represented by the equations

$$n_{t_1}=n_1\left(1-\frac{t}{t_1}\right)$$

etc.

in which n_{t_1} represents the number of cells in prophase calculated at time t after the commencement of the diminution in the prophase figures; it is supposed that the time of administration of the dose of radiation is small.

The diminution in the number of cells in mitosis will be represented by

$$\sum_{r=1}^{4} n_{t_r}=\sum_{r=1}^{4} n_r\left(1-\frac{t}{\sum_{r=1}^{4} t_r}\right)$$

Thus we may write

$$\frac{d}{dt}\left(\frac{n_{t_1}}{n_1}\right)=-\frac{1}{t_1}$$

$$\frac{d}{dt}\left[\frac{\sum_{r=1}^{4} n_{tr}}{\sum_{r=1}^{4} n_r}\right]=-\frac{1}{T_1}$$

These results may be represented diagrammatically as in Fig. 18.

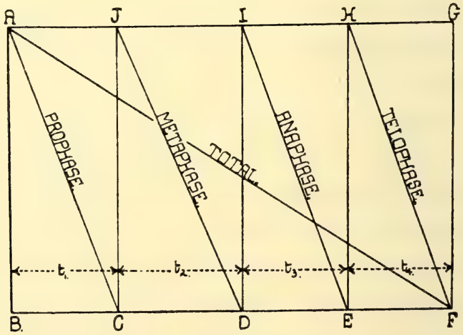

Fig. 18.

If we plot the percentage of cells in the various stages of mitosis along the line A-B, and the time of observation (after the irradiation) along the line B-F, and if the distances B-C, C-D, *etc.*, represent the average duration of prophase, metaphase, *etc.*, we see that the diminution in the number of the various phases of mitosis is represented by the lines A-C, J-D, I-E and H-F. The diminution in the total number of mitoses is represented by the line A-F.

This analytical result bears a striking resemblance to the experimentally determined curves of Kemp and Juul, and we thus have a further piece of evidence in support of the theory of inhibition.

2. Conclusion.

A mathematical analysis of the experimental results of Kemp and Juul, relating to the disappearance of the mitotic phases from irradiated tissue cultures, affords further evidence of the fact that the action of X radiation on mitosis is "inhibitive" and not "destructive".

Section 8.

The Significance of Dosage in the Irradiation of Inter-related Tissues.

In the radiotherapeutic treatment of malignant tumours we are essentially concerned with the irradiation of a nest of malignant cells which are themselves situated in normal healthy structures.

The success of the technique depends upon the fact that the radio-sensitivity of the malignant cells is, in general, greater than that of the surrounding healthy cells; the

ideal technique is the one in which the difference in radio-sensitivities[1] is employed to greatest advantage.

The object of this note is to show that in any such combination of tissues there is always one value of the dosage for which the difference between the biological effects in the two tissues will be a maximum.

1. Analysis.

In problems relating to the irradiation of cells and tissues it is known[(19)(63)-(70)] that the relation between the fractional cellular survival and the dose of radiation administered takes the form:

$$P_1 = e^{-\lambda_1 q} \sum_{r=0}^{n} \frac{(\lambda_1 q)^r}{\lfloor r}$$

where P_1 = the fractional cellular survival,

λ_1 = the probability of absorption of one quantum of energy in the sensitive zone or organ when unit quantity of radiation is administered,

q = the dose of radiation administered,

$n + 1$ = the minimum number of absorbed quanta required to destroy (or otherwise modify) a cell.

If now we simultaneously irradiate two superimposed or inter-related tissues of different radio-sensitivities, the survival equations in their most general forms may be written:

$$P_1 = e^{-\lambda_1 q} \sum_{r=0}^{n} \frac{(\lambda_1 q)^r}{\lfloor r} \qquad \text{.........................(1)}$$

$$P_2 = e^{-\lambda_2 q} \sum_{r=0}^{m} \frac{(\lambda_2 q)^r}{\lfloor r} \qquad \text{.........................(2)}$$

where $\lambda_1 > 0$

and $\lambda_2 > 0$.

---

[1] This difference in sensitivities is technically known as the radio-sensitive interval.

If y represents the difference between the biological effects in the two tissues, we have:

$$y = e^{-\lambda_1 q} \sum_{r=0}^{n} \frac{(\lambda_1 q)^r}{\lfloor r} - e^{-\lambda_2 q} \sum_{r=0}^{m} \frac{(\lambda_2 q)^r}{\lfloor r}$$

and $$\frac{dy}{dq} = y^1 = -\lambda_1 e^{-\lambda_1 q} \frac{(\lambda_1 q)^n}{\lfloor n} + \lambda_2 e^{-\lambda_2 q} \frac{(\lambda_2 q)^m}{\lfloor m}$$

Now when $q = 0$

$y = 0$

and as $q \rightarrow \infty$

$y \rightarrow 0$

therefore y^1 must vanish at least once between 0 and ∞ and $y^1 = 0$

when

$$e^{(\lambda_2 - \lambda_1)q} = \frac{\lfloor n \lambda_2^{m+1}}{\lfloor m \lambda_1^{n+1}} q^{m-n}$$

Several cases now arise for consideration.

Case 1. $\lambda_1 > \lambda_2$, $m > n$.

In this case we see that $e^{(\lambda_2 - \lambda_1)q}$ decreases from 1 to 0 as q increases from 0 to ∞ and $\frac{\lfloor n \; \lambda_2^{m+1}}{\lfloor m \; \lambda_1^{n+1}} q^{m-n}$ increases from 0 to ∞ as q increases from 0 to ∞.

Hence there exists a unique ξ, such that

$y^1(\xi) = 0$

and in this case y^1 has only one zero and

$$y \neq 0.$$

The graph of y as a function of q is shown in Fig. 19. It is seen that as the dose of radiation increases from 0 to infinity the difference between the biological effect in the two tissues decreases from zero, attains a minimum value and then increases again to zero. The value of q, producing the maximum difference in biological effects,

can be easily calculated in terms of the characteristics of the irradiated tissues.

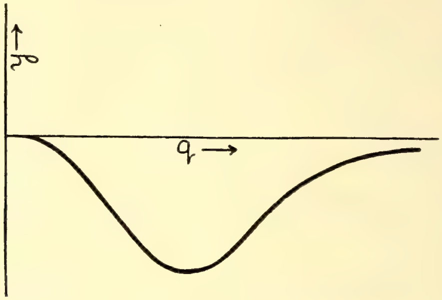

Fig. 19.

Case 2. $\lambda_1 > \lambda_2$, $m = n$.

In this case it is clear that

$$\frac{\underline{|n}}{\underline{|m}} \cdot \frac{\lambda_2^{m+1}}{\lambda_1^{n+1}} < 1$$

and there exists a unique solution as in Case 1.

Case 3. $\lambda_1 < \lambda_2$, $m > n$.

In this case $e^{(\lambda_2 - \lambda_1)q}$ increases from 1 to ∞ as q is increased from 0 to ∞ and it ultimately surpasses any power of q. We also know that y^1 must have at least one zero value, and hence the curves

$$y_1 = e^{(\lambda_2 - \lambda_1)q}$$

and

$$y_2 = \frac{\underline{|n}\ \lambda_2^{m+1}}{\underline{|m}\ \lambda_1^{n+1}} q^{m-n}$$

must cross an even number of times. Thus y^1 has an even number of zeros and the graph of y must cross the axis of q at least once, and when $q = \infty$, y is clearly positive.

This case is represented diagrammatically in Fig. 20. It is seen that as q increases from 0 to ∞, the difference between the biological effects decreases from zero, attains

a minimum value, increases through zero to a maximum value, and then decreases again to zero. This result means that the survival curves given by equations (1) and (2) must cross, and, as before, the values of q pro-

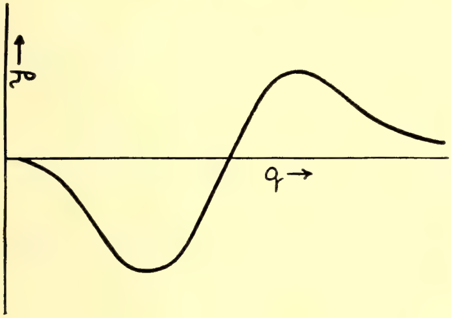

Fig. 20.

ducing the maximum or minimum difference in biological effects can be easily calculated in terms of the characteristics of the irradiated tissue.

Case 4. $\lambda_1 < \lambda_2$, m = n.

From the previous work it is clear that in this case, y^1 has only one zero value and the relation between y and q can be represented diagrammatically as in Fig. 21.

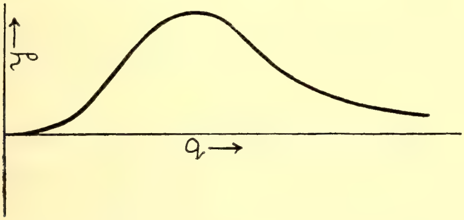

Fig. 21.

Case 5. $\lambda_1 = \lambda_2$, $m > n$.

In this case we see that

$$y^1 = 0$$

when $$\frac{\underline{|n}}{\underline{|m}} \frac{\lambda_2^{m+1}}{\lambda_1^{n+1}} q^{m-n} = 1$$

and a unique solution again clearly exists. The relation between y and q can be represented diagrammatically by Fig. 22.

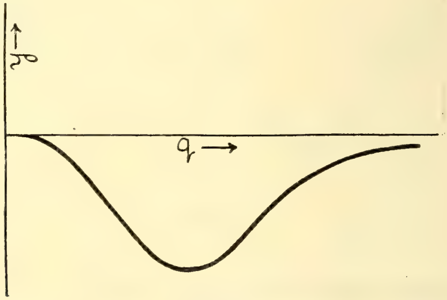

Fig. 22.

Case 6. $\lambda_1 = \lambda_2$, $m = n$.

In this case it is clear that

$$y \equiv 0.$$

2. Discussion.

An inspection of the diagrams shows us that, for any possible combination of cells or tissues (except that combination of identical tissues considered in Case 6), we can always find at least one value of the dosage, for which the difference between the survivals will be a maximum or a minimum.

Before it is possible to determine this dosage, we must know the sensitivities of the tissues in question. Very little precise information of this nature is available at present for human tissues, but the determination of sensitivities is a fairly straightforward problem.

In view of the possible importace of this result in the radiotherapeutic treatment of malignant disease, it may be important to stress the fact that no hypotheses have been introduced into the above analysis. It is based entirely on experimental facts.

The result follows, in a general way, from simple considerations. The shape of the curve relating dosage and quantitative biological effects in any one tissue is always sigmoid. The difference between the quantitative biological effects of the radiation in inter-related tissues will, therefore, be graphically represented by the algebraic difference between two such sigmoid curves. This difference curve will always be of the same general shape as the curves already considered.

3. Conclusion.

An analytical study of the quantitative effects of radiation on cellular survival in inter-related tissues leads to the conclusion that there is always one value of the dosage for which the difference between the biological effects in the two tissues will be a maximum.

PART II.

The Mitotic Activity of Jensen's Rat Sarcoma and its Modification by X Rays.

Previous Work.

The fundamental investigations at the beginning of this century into the transplantability of malignant tumours opened wide vistas of the practicability of studying the influence of various factors on tumours.

Among the first to carry out such studies was Jensen,[71] whose pioneering work in this field is known all over the world.

Most experimental work on the influence of radiations upon malignant tumours has been based on the irradiation of transplanted tumour tissue *in vivo* or *in vitro*, followed by transplantation for indication of the effect. While the earlier investigators were generally concerned with the histological changes produced by different doses of radiation, the more recent experiments have mainly centred around the problems relating to the lethal or sterilisation doses of tumours, the direct and indirect action of radiations on malignant tissues, and the experimental production of immunity. The results of these experiments are on the whole rather inconclusive, and a consideration of the extensive literature would take us too far afield.

The problems of mitotic activity in malignant tumours and the modification produced by radiations have not received very much attention.

The significance and possible importance of the mitotic index[1] in radiotherapy were studied by McConnell[(72)] in 1908; McConnell made some observations on the relation between growth rate and mitotic activity in human cancers. By direct counting in a definite number of microscopic fields, he estimated the mitotic activity of each tumour, and found that this number was not a dependable index of the tumour's growth rate. The author emphasised the impracticability of this index in therapeutic work.

In 1919 Russ[(73)] studied the occurrence of mitosis in Jensen's rat sarcoma, and found that the most rapidly growing tumours had the highest mitotic index. In 1926, however, and in collaboration with Mottram and Scott,

---

[1] The mitotic index is defined as the ratio between the number of dividing cells and the number of resting cells as determined by direct counting in a large number of microscopic fields.

Russ[12] came to the conclusion that the most rapidly growing tumours did not necessarily have the highest mitotic index. In my opinion, the results shown in this second paper actually support the earlier view.

The experiments reviewed above were not very critical, because the growth rates were qualitatively described by such terms as "rapid" and "slow", *etc.*

In 1923 De Nabias and Forestier[74] attempted to set up a rational scheme of therapy, based on the mitotic index, but their work was immediately criticised by Holthusen[75] and Laborde[76] on the grounds that the mitotic frequency is disturbed by the irradiation, and that the distribution of mitoses in the neoplasm is irregular.

There is one further significant series of experiments that may appear to support the original view of McConnell.

White and Loeb,[77], Bashford, Murray and Bowen,[78] and Woglom[79] have shown that a regressing neoplasm can be successfully transplanted. Woglom stated that division figures could be found up to the very edge where healthy tumour adjoins necrosis. These experiments mean that even when the growth rate of a tumour is negative the mitotic activity in the peripheral portions may be considerable.

I have not been able to find any other material contribution to the study of mitotic activity in malignant tissues.

The study of the modifications produced in the mitotic activity by radiations has likewise attracted little attention. The only important contributions to the subject have been made by Lacassagne and Monod,[37]

Dustin,[41][42] and Mottram, Scott and Russ,[12] and have already been noted in Part I.

Section 1.

The Occurrence of Mitosis in Jensen's Rat Sarcoma.

1. Growth Rate Phenomena in Experimental Animal Tumours.

The experimental propagation of malignant new growths leads to an apparently continuous proliferation, which is merely artificially divided up by the process of transference to successive hosts. The limits of growth are not attained in any one animal, and transplantation again becomes necessary after intervals which vary according to the rate of growth of the tumour, or to the degree in which the animal suffers from intercurrent disease. Thus the time of transplantation does not possess the importance of a natural starting point for the growth as such, neither does it coincide with a terminal stage of the growth with which the transplantation is effected.

Alterations in the rate of growth of a tumour are caused by:

(1) Transference from one strain of animal to another.

(2) Transference from young to old animals of the same race or *vice versa*.

(3) Variation in the site of implantation of the cancerous tissue.

(4) Variation in the amount of tissue introduced and in the manner of introducing it.

(5) Variation in the characters of the tumour cells themselves.

The growth rate characteristics of a neoplasm that has been grafted into a particular animal is the immediate resultant of:

(1) Cellular division.
(2) Cellular hypertrophy.
(3) Deposition of intercellular substance.
(4) Degree of vascular engorgement.
(5) Amount of necrosis.
(6) Degree of regression.

The microscopic examination of actively growing non-regressive rat sarcomata of Jensen has convinced me of the fact that the second, third and fourth factors do not make any significant contribution to the increase in volume of the tumour. In such tumours, therefore, the increase in volume is due almost entirely to cellular division.

Let us now determine the growth rate characteristics of such a neoplastic tissue, composed entirely of actively proliferating cells. The only assumption made in the following analysis is that all the cells are in a state of active proliferation.

2. Growth Rate Equation of an Actively Proliferating Tissue.

Let N_t = the number of cells present in the tumour at time,

T_1 = the average duration of cellular division,

T = the average duration of the inter-mitotic period.

We can say that

$$N_t = f(t),$$

and since we know that

$$f(t + T + T_1) = 2f(t),$$

it follows that the growth of such a neoplasm is represented by the simple exponential equation

$$N_t = N_0 e^{\alpha t} \quad \dots\dots\dots\dots\dots\dots\dots\dots (1)$$

in which N_0 is the number of transplanted cells that grow and α is the coefficient of growth rate.

3. Discussion.

We see that if all the cells of a tumour were actively proliferating, its rate of growth would be represented by a simple exponential curve.

That the growth rate curve for the rat sarcoma of Jensen is exponential for many days was found by Russ[80] and later confirmed by me (*vide* Fig. 23). The ultimate departure of the growth curve from the exponential form can therefore be ascribed to the fact that some of the cells have ceased their active proliferation, *i.e.,* the tumour is regressing or becoming necrotic.

Now in such necrotic or regressing tumours it is clear that the growth rate of a small part is no longer identical with the growth rate of the whole tumour. This is a very important consideration, and explains the difficulties encountered in the attempts that have so far been made to correlate the mitotic index and the growth rate of a whole tumour.

The mitotic index is necessarily determined in microscopical sections; it varies with the growth rate of the part from which it was taken. The growth rate of a part can only be identified with the growth rate of the whole tumour, when the latter is non-necrotic and non-regressive, *i.e.,* when its growth rate curve is exponential in form at the time of taking the section.

We thus see why:

(1) The mitotic index is not necessarily an infallible index of the growth rate of a whole neoplasm.

(2) A tumour with negative growth rate may contain many mitoses, *i.e.*, a regressing neoplasm may be successfully transplanted.

4. The Relation Between Mitotic Index and Coefficient of Growth Rate in an Actively Proliferating Neoplasm.

In an actively proliferating neoplasm the growth rate equation takes the form

$$N_t = N_0 e^{\alpha t}$$

If now we represent the number of cells in division at time t by the symbol n_t, we have

$$\frac{n_{t_1}}{N_{t_1}} = \frac{\left(\frac{dN_t}{dt}\right)^{T_1}_{t=t_1-T-T_1}}{N_{t_1}} = \frac{\alpha}{2} T_1 \quad \ldots\ldots\ldots\ldots (2)$$

or

$$\frac{n_t}{N_t} = 0{\cdot}35 \frac{T_1}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

These results show that, in such a neoplasm, the mitotic index should be proportional to the product of the coefficient of growth rate and the average duration of mitosis.

I will now describe some experiments that were made in order to test the validity of this conclusion.

5. Experimental.

A series of rats were inoculated with Jensen's rat sarcoma according to one or other of the two following techniques.

In the first method a tumour was removed aseptically from a rat, minced into very fine pieces and placed in a sterile petri dish, with a few drops of sterile saline.

The experimental animals were anæsthetised, epilated and swabbed with alcohol, over a small area, on the lower part of the abdomen.

The tumour material was then introduced subcutaneously into the experimental animals with a Bashford needle and syringe, and carefully pushed up into the axilla.

In the second method a small incision, about 1 cm. in length, was made through the epilated skin of a rat; a blunt instrument was introduced into this incision and carefully pushed up into the axilla. A piece of tumour material, about $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$ c.cm., was then introduced with fine forceps and the incision closed with sutures.

Charts were then prepared showing the daily increase in volume of each tumour. A typical result is reproduced in Fig. 23.

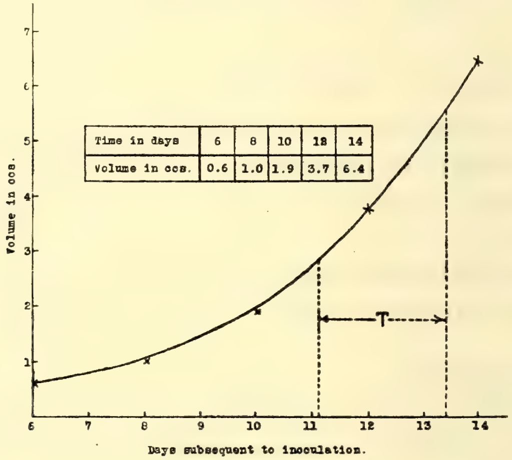

Fig. 23.

If the shape of the tumour was perfectly regular, the volume could be accurately determined by direct measurement.

When the shape of the tumour was irregular, the tumour was held up from the body of the rat and a

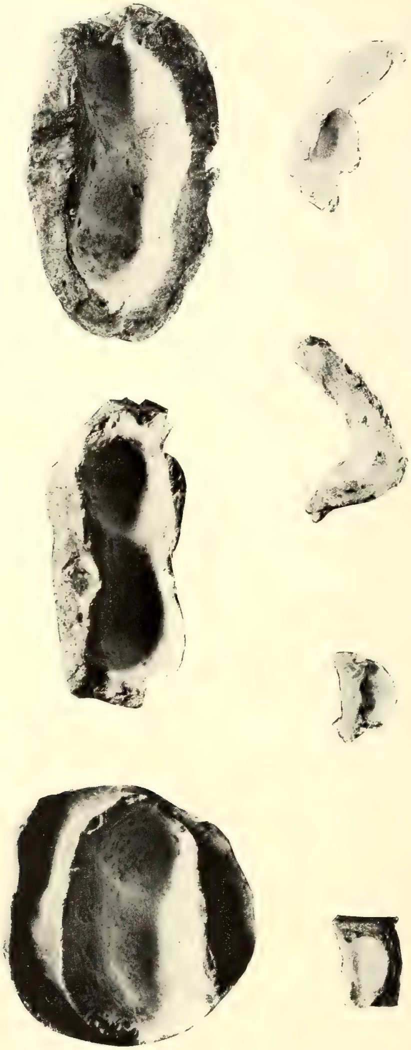

Plate I.

complete external cast was made in plaster of Paris. The cast could be removed in two sections and the volume determined by measuring the amount of water required to fill the two portions. Portions of external casts obtained for tumours of different sizes are shown in Plate I.

In some cases the volume of the tumour was directly determined by a simple water displacement method.

6. Results.

(*a*) Correlation between relative frequency of mitosis and growth rate.—An examination of the charts revealed a considerable variation in the growth rates of the different tumours; the typical tumour, however, was one which doubled its volume in about four days, as also found by Russ.[73]

A selection was made of progressively growing tumours that continuously doubled their volumes every two, four and six days respectively. Thus three series of experimental material were obtained, and this procedure also ensured the exponential form of the growth curve for the selected tumours.

The average time T taken for a tumour to double its volume could be directly determined from the growth chart, as shown in Fig. 23, and the coefficient of growth rate was found from the relation

$$\alpha = \frac{0 \cdot 6932}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The rats were then killed, and small portions of tumour taken from different places were fixed with Zenker's fluid, cut into section and stained with iron alum.

Each tumour was microscopically examined for mitotic content. The number of dividing cells contained in 250

fields, chosen at random, was obtained by direct counting, and the results of this enumeration are shown in Table 11.

TABLE 11.

	$\alpha=\frac{\log_e 2}{48}$	$\alpha=\frac{\log_e 2}{96}$	$\alpha=\frac{\log_e 2}{144}$
Number of cells in division per 50 fields.	73 69 65 81 77	37 44 35 46 39	18 27 17 30 20
Total	365	201	112
Mean per 50 fields ..	73	40	22

It is seen that, to a first approximation, the relative frequency of occurrence of mitosis in these tumours is directly proportional to α, the coefficient of growth rate.

(*b*) The frequency of mitosis.—An examination of fixed specimens was made from the point of view of mitotic index.

The number of cells (dividing and resting) contained in any microscopic field was determined by direct counting with a squared eyepiece. The average figure obtained for ten fields was 102 per field. The results are shown in Table 12.

If this result is used in conjunction with the figures contained in Table 11, we can directly determine the mitotic index $\left(\frac{n_t}{N_t}\right)$ for any particular tumour.

By a rearrangement of equation (2) we see that

$$T_1 = \frac{2}{\alpha}\left(\frac{n_t}{N_t}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

and if in this equation we substitute the appropriate values of α and $\frac{n_t}{N_t}$ for the different tumours, we find the very interesting result that T_1 is approximately equal to two hours. This means that the average duration of division is independent of the growth rate of the tumour.

TABLE 12.

	Number of cells per field.
	105
	110
	98
	101
	97
	108
	89
	91
	103
	110
Total ..	1,022
Average per field	102

It thus follows that the variations in the growth rates of individual neoplasms of the same type depend exclusively upon modifications in the average duration of the inter-mitotic period.

7. Conclusions.

(1) The relative frequency of occurrence of cellular divisions in non-necrotic and non-regressing

tumours of Jensen's rat sarcoma is proportional to the growth rate of the whole tumour.

(2) The average duration of the process of cell division in these tumours is independent of the growth rate.

(3) The variations in the growth rates of individual tumours of Jensen's rat sarcoma depend exclusively upon modifications in the average duration of the inter-mitotic period.

Section 2.

The Effect of X Radiation upon Cellular Division in Jensen's Rat Sarcoma.

The success of quantitative experiments upon mitosis in irradiated neoplasms depends ultimately on our ability to select a series of tumours with the same mitotic index.

In their experiments on the effects of β radiation on mitosis in Jensen's rat sarcoma, Mottram, Scott and Russ[12] attempted to control the variation in the mitotic index by growing an experimental and control tumour in the same animal. Even under these conditions a 2:1 variation in mitotic index was recorded.

Now that we have established a relation between the growth rate of a tumour and its mitotic index, this difficulty can be very easily overcome. The selection of experimental and control tumours must be based on an examination of the growth rate charts for the individual tumours.

I will now describe some experiments that were undertaken in order to study the quantitative effects of approximately homogeneous X radiation on mitosis in Jensen's rat sarcoma.

1. Experimental.

Throughout the following experiments I have used a sarcoma that had been propagated in the same strain of rat for a period of 10 years. The growth rate of these tumours was very uniform. Each tumour doubled its volume in the space of about four days.

In each experiment six tumours were selected, three of which were submitted to a measured dose of approximately homogeneous radiation while the remaining three served as controls. Care was taken to protect the body of the rat from the rays, so that the tumours only were irradiated.

The irradiations were made with a Coolidge tube, immersed in a bath of oil, and excited with a Gaiffe-Gallot generator, working at 90 kilovolts.

The rays were filtered by $\frac{1}{10}$th mm. tungsten and 3 mm. aluminium, and the dose administered was measured with a Solomon Ionometer.

After the termination of each irradiation the tumours were allowed to remain undisturbed in the body of the rat for a period of two hours, *i.e.,* for a length of time equal to the average duration of mitosis. At this stage the irradiated and control animals were killed, small portions of each tumour were excised and fixed in Dubosq-Brasil's fluid. These pieces of tumour were finally made into section, stained with iron hæmatoxylin and examined microscopically for mitotic figures.

The number of dividing cells in 170 different fields was enumerated for each tumour (irradiated and control), and in this way the mitotic survival (*vide* Part I) was obtained for each dosage. The results of the experiment are shown in Table 13 and represented graphically in Fig. 24.

TABLE 13.

Dose in R units ..	0	90	150	300
Number of dividing cells in 170 fields	193	143	70	62
Mitotic survival ..		74%	36·3%	32·1%

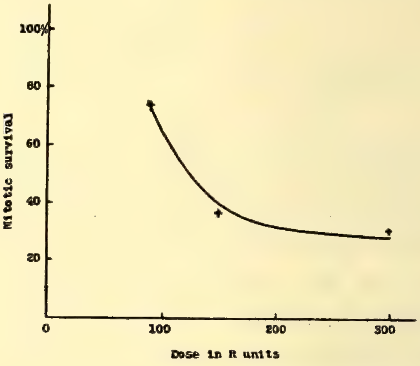

Fig. 24.

From these results we see that:

(1) Two hours after the administration of 300 R units the mitotic survival is reduced to about 30%.

(2) The mitotic survival dosage curve is very flat in the vicinity of 300 R. And the disappearance of a few more mitoses demands a relatively large increase of dosage.

2. Discussion.

Working with radiation produced under a potential difference of 40 cms. (between points) and filtered by

5 mm. aluminium, Samssonow[81] found that the sterilization dose for this tumour was about 5,580 R.

There is thus a very considerable difference between the amount of radiation required to sterilise the tumour and that required to inhibit the majority of the mitoses. (The term "inhibit" is here used with all appropriate reservations.)

In the work already referred to[12] Mottram, Scott and Russ found that, one hour after exposure to 180 millicuries of radium emanation for 30 seconds, or to 30 milligrams of radium bromide for 30 minutes, the mitotic survival in Jensen's rat sarcoma was reduced to about 20%. This result has been taken by Juul[11] to indicate a stronger effect from the greater intensity. When the results are analysed they are found to mean that the administration of either one-tenth of a lethal dose or one-half of a lethal dose produces a mitotic survival of about 20%, one hour after the termination of the irradiation. I would like to suggest that the result is not necessarily anything more than a testimony to the flatness of the survival dosage curve in the vicinity of a 20% survival.

3. Conclusions.

1. The amount of radiation required to sterilise the rat sarcoma of Jensen is very much greater than that required to inhibit the majority of the cells from dividing.

2. Two hours after the administration of 300 R units the mitotic survival is reduced to about 30%.

3. The mitotic survival dosage curve is very flat in the vicinity of a dose equal to 300 R units and the inhibition of a few more mitoses demands a relatively large increase of dosage.

Mathematical Notes.

Note 1 (page 100).

We have

$$\frac{\Sigma S}{\frac{dN}{dt}}=\int_{t-T_1}^{t} e^{-\alpha\lambda t}\sum_{r=0}^{n-1}\frac{(\alpha\lambda t)^r}{\lfloor r}.\ dt.$$

$$=\frac{1}{\alpha}\int_{\alpha t-\alpha T_1}^{\alpha t} e^{-\lambda t}\sum_{r=0}^{n-1}\frac{(\lambda t)^r}{\lfloor r}dt$$

$$=\frac{t}{q}\int_{q-q\frac{T_1}{t}}^{q} e^{-\lambda t}\sum_{r=0}^{n-1}\frac{(\lambda t)^r}{\lfloor r}.\ dt$$

Now, as t increases, the factor outside the integral increases, the range of integration decreases, and the integrand is a decreasing function of t. Hence if A is the mean value of the integrand in the range of integration we have

$$\frac{\Sigma S}{\frac{dN}{dt}}=\frac{t}{q}\ .\ q\frac{T_1}{t}\ .\ A$$

$$=T_1A$$

and the mean value of the integrand decreases as t increases.

Note 2 (page 115).

We have

$$\frac{\Sigma S_1+\Sigma S_2}{\frac{dN}{dt}}=t_2e^{-\lambda q}\sum_{r=0}^{n-1}\frac{(\lambda q)^r}{\lfloor r}+\frac{t_1}{\alpha t_1}\int_{\alpha t_3}^{\alpha t_1} e^{-\lambda t}\sum_{r=0}^{n-1}\frac{(\lambda t)^r}{\lfloor r}\ .\ dt$$

where $\alpha t_1 = q =$ constant

and $\alpha t_3=q\frac{t_3}{t_1}$

Thus $$\frac{\Sigma S_1+\Sigma S_2}{\frac{dN}{dt}}=t_2F(q)+\frac{t_1}{q}\left(q-q\frac{t_3}{t_1}\right)F(\xi)$$

where $q>\xi>q\frac{t_3}{t_1}$

now $F(t)$ is a decreasing function of t and $t_1 + t_2$ is constant. Thus when t_2 is increased t_1 is decreased and the mean value $F(\xi)$ of $F(t)$ in the range of integration is decreased.

Now if t_2 is increased by δt we get

$$\frac{\Sigma S_1+\Sigma S_2}{\frac{dN}{dt}}=(t_2+\delta t)F(q)+(t_1-\delta t-t_3)F(\xi^1)$$

where $q>\xi^1>\xi>q\frac{t_3}{t_1}$

The increase in $\frac{\Sigma S_1+\Sigma S_2}{\frac{dN}{dt}}$ is then

$$\delta tF(q)-\delta tF(\xi^1)+(t_1-t_3)\{F(\xi^1)-F(\xi)\}$$

and since

$$F(q) < F(\xi^1)$$

and

$$F(\xi^1) < F(\xi)$$

it follows that the increase is negative.

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Explanation of Plate I.

Portions of external casts obtained for tumours of different sizes.

THE CHEMICAL CHANGES INVOLVED IN THE FORMATION OF AMINOAZO COMPOUNDS.

PART I.

By JOHN CAMPBELL EARL, D.Sc., Ph.D.,
and NORMAN FREDERICK HALL, B.Sc.

(Read before the Royal Society of New South Wales, June 1, 1932.)

The question as whether diazoaminobenzene is necessarily formed as an intermediate stage in the production of aminoazobenzene arises as a natural sequence of the investigations already described on the behaviour of diazoaminobenzene with acids (this *Journal*, 1929, **63**, 89; 1930, **64**, 96). Although at one time the view was widely held that a migration of the diazo group from its point of attachment to nitrogen to the para position in the nucleus was the change involved in the conversion of diazoamino into aminoazobenzene, it has recently become increasingly evident that a better explanation is to postulate a fission of the diazoamino compound and a re-combination of the fragments to yield the aminoazo derivative. It has been shown by Rosenhauer (*Berichte*, 1931, **64**, 1438) that the formation of benzenediazoamino-azobenzene (Earl, this *Journal*, 1930, **64**, 96) during the conversion is probably due to aminoazobenzene coupling in the diazoamino sense with free benzenediazo salt in the reaction mixture. This explanation is obvious in view of the facility with which Rosenhauer found such a

reaction to take place, but it is curious to note that Vignon (*Comptes rendus,* 1905, **140**, 91), who tried to bring about this type of coupling, was unsuccessful in doing so. There is no doubt, however, that the "fission" theory accounts better for the formation of benzene diazoaminoazobenzene than any modification of the "migration" theory.

The experiments described in the present paper were originally initiated with a view to obtaining some information as to why diazoaminobenzene is formed from diazo compound and amine under some conditions and aminoazobenzene under others. The answer to this question is not yet forthcoming, but observations have been made which throw considerable light on the fundamental reactions of the diazotisation process.

In methanol as solvent, at 0°-3° C., two molecular proportions of aniline hydrochloride and one of sodium nitrite were found to react to give some diazoaminobenzene, but the greater part of the aniline apparently remained unattacked. At 14°-16° C., however, the same substances, present in the same proportions, led to the production of a good yield of aminoazobenzene. Such a marked difference in behaviour by the variation of the temperature factor alone suggests the possibility that it is not two competing reactions of different velocities between diazo compound and amine which are involved, but rather an intramolecular change of one of the reactants between 3° C. and 16° C. The diazo salt, notoriously an unstable molecule, is naturally the reactant to be suspected of such a change.

A statement by Cain (*Chemistry and Technology of the Diazo-Compounds,* 1920 edition, p. 89) that

nitrosamines and primary amines condense to give diazoamino compounds was first scrutinised in this connection. The implication of such a statement, if accurate, is that the diazoamino coupling might depend on the presence in the reaction mixture of the nitrosamine form of a diazo oxide, the reaction proceeding thus:

$$C_6H_5NH.NO + C_6H_5NH_2 \rightarrow C_6H_5NH.N:NC_6H_5 + H_2O.$$

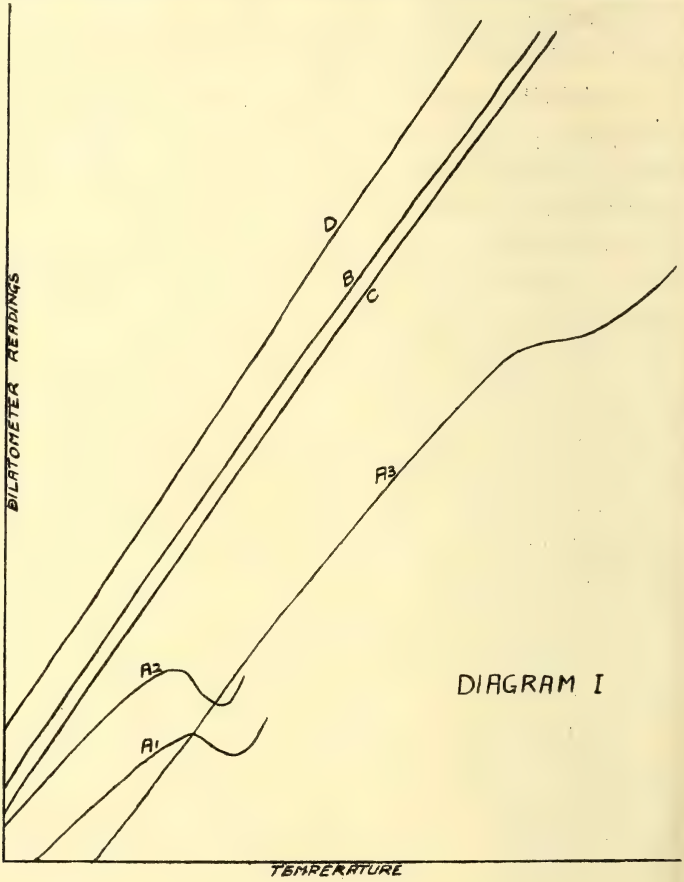
However, phenyl benzyl nitrosamine showed no tendency whatever to react with aniline under acidity conditions usually favourable to the formation of diazoamino compounds, so that, in all probability, the existence of a nitrosamine in the reaction mixture is not the cause of the diazoamino coupling.

An intramolecular change occurring in one of the reactants taking part in a coupling might possibly bring about a sudden, if small, change in the volume of the reaction mixture. On this account, therefore, a methanol solution of aniline hydrochloride (2 mols) and sodium nitrite (1 mol), as previously employed, was heated slowly in a dilatometer over a range of temperature from 7° to 17° C. Several experiments were carried out, and in every case a marked discontinuity in the volume-temperature curve was observed (Diagram I[1], curves A_1, A_2, A_3), there being usually a definite contraction in volume over a fraction of a degree. The point at which the discontinuity occurred appeared to be influenced by small variations in the composition of the reaction mixture and in the conditions of experiment. Also, the most pronounced change in the colour of the solution,

[1] In Diagrams I and II the curves are not plotted to equivalent co-ordinates for temperature and dilatometer readings, it being desired to emphasize the form of the curve rather than a mathematical relationship. The essential numerical data are given in the table at the end of the paper.

indicating the formation of aminoazobenzene, took place at the temperature at which the contraction occurred.

In amplification of these preliminary observations, further experiments were made on the same plan. It



was found that when equimolecular proportions of aniline hydrochloride and sodium nitrite were used, the discontinuity in the volume-temperature curve did not appear or, possibly, occurred at a higher temperature (Diagram I, curve B). Methanol solutions of aniline

hydrochloride alone and of benzene diazonium chloride, prepared according to the directions of Hantzsch (*Ber.*, 1901, **34**, 3338) alone, showed no discontinuity (curves C and D). On the other hand, methyl aniline hydrochloride or benzyl aniline hydrochloride when mixed with sodium nitrite in the proportion of two mols of the hydrochloride to one of the nitrite showed similar behaviour to aniline hydrochloride itself (Diagram II).

Some chemical evidence also, which must be taken into consideration in framing an explanation of the above

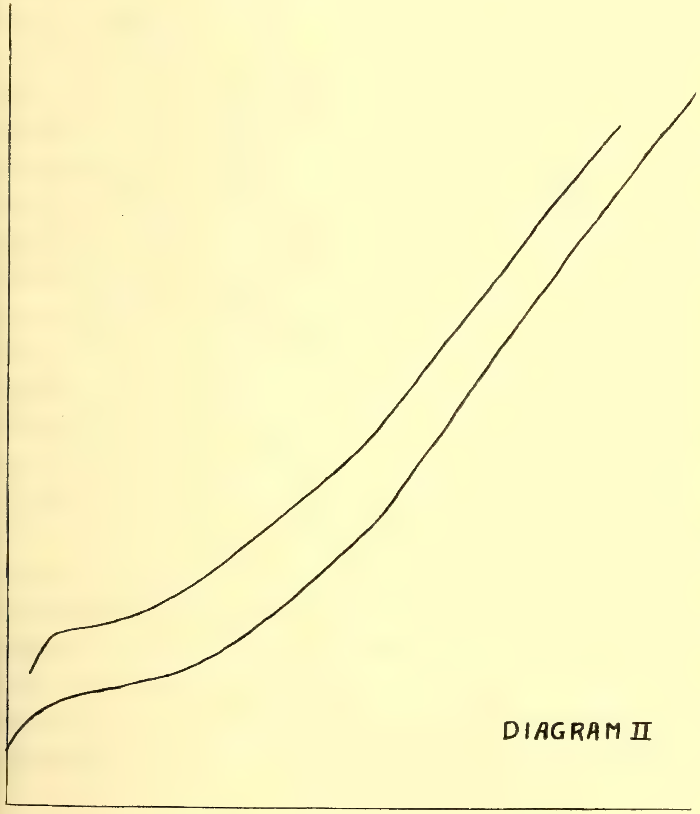


DIAGRAM II

results, is forthcoming. Equimolecular proportions of aniline hydrochloride and sodium nitrite dissolved in methanol at 0° C. yield a solution which when poured into alkaline β-naphthol gives no coloration. The addition of one drop of hydrochloric acid to a quantity of such a solution is sufficient to confer upon it the property of giving the usual diazo reaction with β-naphthol.

It is to be expected, and no doubt has been generally assumed, that the first action between aniline and nitrous acid gives aniline nitrite, which then undergoes further change. The nitrites of a number of organic bases have been isolated from time to time and examined (Bamberger, *Berichte,* 1889, **22**, 771, *Annalen,* **257**, 19; Noyes, *Am. Chem. Jour.*, 1893, **15**, 539; Wallach, *Annalen,* **353**, 318; also a number of later papers by Ray and Rakshit, Neogi and others). The primary amine nitrites are decomposed on heating, more or less readily, nitrogen and the corresponding hydroxy compound being produced, while the secondary amine nitrites yield nitrosamines. Although most of these observations were made on aliphatic and alicyclic amines, there is every reason to believe that aromatic amines behave in essentially the same manner (Wallach, *loc. cit.*) The familiar existence of aromatic diazo compounds indicates merely that compounds of this type are more stable in the aromatic than in the aliphatic series.

Our knowledge of the properties of nitro and nitroso groups leads us to expect that the amine nitrites would tend to undergo change into compounds of the type represented by Formulæ III and IV, the former being derived from a primary and the latter from a secondary amine. This change involves merely the transference of hydrogen from nitrogen to oxygen atoms.

III. R.NH.N(OH)$_2$. IV. $\begin{matrix}R\\R^1\end{matrix}\!>$N.N(OH)$_2$.

Loss of water from such intermediate products could lead in either case to the formation of a nitrosamine, but in the case of the primary amine the formation of a diazo compound, or of nitrogen and a hydroxy compound is also possible.

All the experimental evidence now brought forward supports the conclusion that the volume change indicated by the dilatometer readings is brought about either by the change of an amine nitrite into the typical intermediate, or by loss of water from the latter. The change requires, apparently, the existence of a certain hydrogen ion concentration in the reaction mixture, this being provided by the excess of amine hydrochloride. It is noteworthy that methylamine hydrochloride (2 mols) and sodium nitrite (1 mol) do not give the characteristic volume-temperature curve, but here the strength of the base may militate against the development of a sufficiently high hydrogen ion concentration. In this connection, reference must be made to the work of Taylor (*Jour. Chem. Soc.*, 1928, 1099) on the action of nitrous acid on amines. He found that equimolecular proportions of methylamine and nitrous acid do not react with destruction of the amine at 25° C. Excess of nitrous acid, however, brought about the disappearance of the methylamine at a measurable rate, that is, in the light of the present work, the hydrogen ion concentration had been increased sufficiently to allow of the rearrangement of the amine nitrite. The apparently contradictory effect of the addition of a relatively large quantity of sulphuric acid in retarding the decomposition of the methylamine, is readily explained by the supposition that

much of the amine nitrite was thereby converted into the sulphate of the amine.

This work is being continued, with special reference to the isolation of aniline nitrite, and the investigation of its behaviour.

Experimental.

The Interaction of Aniline and Sodium Nitrite in Methanol Solution.

At 0-3° C.

Aniline hydrochloride (10 grams) was dissolved in methanol (80 cc.) and cooled to 1° to 3° C. A solution of sodium nitrite (2·8 grams) in methanol (200 cc.) was added with stirring over a period of 65 minutes. At no time during this period was any definite red coloration with alcoholic alkali observed. The reaction-mixture was poured into ice-cold, dilute caustic soda solution, and after standing for some time the precipitated yellow solid (1·1 grams) was filtered off and identified as diazoaminobenzene. The alkaline solution contained aniline (bleaching power test).

At 14-16° C.

The same proportions of the reagents were taken, the sodium nitrite solution being added to the aniline hydrochloride solution over a period of $1\frac{1}{4}$ hours. The temperature was maintained at 14°-16° C. during the addition and for a further $2\frac{3}{4}$ hours. During the greater part of this period samples of the reaction-mixture produced the characteristic red colour with alcoholic alkalies. When this reaction was no longer shown, the mixture was poured into ice-cold dilute caustic soda solution and extracted with benzene. By passing hydrochloric acid gas into the benzene solution, the aminoazobenzene was precipitated as its hydrochloride (4·7 grams).

Attempted Condensation of N-nitrosobenzylaniline (Phenyl Benzyl Nitrosamine) with Aniline.

(*a*) The nitrosamine (1 gram) and aniline (0·45 gram) were dissolved in alcohol (8 cc.) and the solution allowed to stand for 20 hours. After pouring into water, the precipitated material was filtered off and identified as unchanged nitrosamine.

(*b*) An alcoholic solution of the same composition as above was poured into a solution of acetic acid (2 cc.) and potassium oxalate (8 grams) in water (160 cc.). The mixture was stirred thoroughly for six hours, after which time the solid was filtered off and identified as unchanged nitrosamine (0·95 gram).

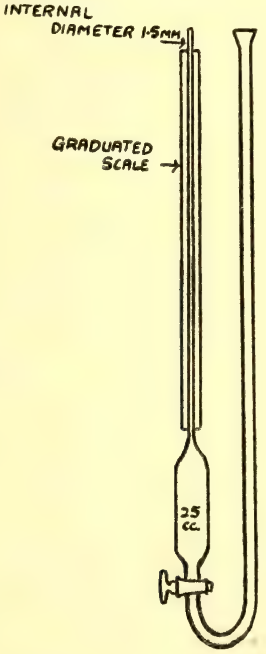


DIAGRAM V

Dilatometric Measurements on Reaction-Mixtures Containing Amine-Hydrochlorides and Sodium Nitrite.

A simple dilatometer of the type illustrated in Diagram V was employed. The instrument with the tap open was immersed in a bath brought to the initial temperature of the experiment. After a few minutes the cold solution (all the mixtures were prepared at about 0° C.) to be investigated was poured in, and when the volume had become constant the tap was closed. Thereafter, readings on the graduated limb of the dilatometer were taken at one-tenth or one-twentieth of a degree intervals as the temperature rose. Usually the starting and finishing temperatures were below that of the laboratory and no external heating was necessary, but in a few instances the temperature was raised in small steps by the addition of hot water.

The following table summarises the composition and other data of the mixtures to which the curves in Diagrams I and II refer:

	M.	R.	S.	T_1.	T_2.	T_3.	T_4.	H_1.	H_2.
			Mins.	° C.	° C.	° C.	° C.		
I A_1	0·379	2/1	12·5	10·0	12·0	13·05	13·1	0·08	0·03
I A_2	0·379	2/1	118·0	9·8	11·4	12·35	12·35	0·07	0·04
I A_3	0·432	2/1	5·0	3·1	10·3	11·9	12·5	0·09	0·07
I B	0·216	1/1	5·0	7·4	—	—	19·9	0·045	0·25
I C	0·331	—	5·0	6·3	—	—	19·8	0·09	0·03
I D	0·16	—	—	4·2	—	5·2	10·0	0·07	0·04
II A	0·451	2/1	5·0	9·0	9·4	—	17·0	0·06	0·015
II B	0·349	2/1	3·5	4·3	4·6	—	11·1	0·08	0·03

M —Molar concentration of amine hydrochloride.
R —Molar ratio of amine hydrochloride to nitrite.
S —Time elapsing between mixing and the commencement of readings.
T_1—Temperature at first reading.
T_2—Temperature at which a marked change in expansion rate was first observed.
T_3—Temperature at which evolution of gas was first observed.
T_4—Temperature at final reading.
H_1—Temperature rise per minute at commencement.
H_2—Temperature rise per minute at finish.

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A NOTE ON THE ACTION OF TITANIUM TETRACHLORIDE ON TETRACETYL-β-d-GLUCOSIDO-GLYCOLLIC ESTER.

By Thelma Muriel Reynolds, M.Sc.
(Communicated by Professor J. C. Earl.)

(Read before the Royal Society of New South Wales, June 1, 1932.)

An attempt to prepare tetracetyl-α-d-glucosido-glycollic ester by means of the action of titanium tetrachloride on the corresponding β-glucoside following the method evolved by Pacsu (*Ber.*, 1928, **61**, 1508; *J. Amer. Chem. Soc.*, 1930, **52**, 2563) was unsuccessful, acetochloroglucose, which was obtained in 71% yield, being the only substance isolated from the reaction. Tetracetyl-β-d-glucosido-glycollic ester behaves, therefore, in the same manner as the fully acetylated sugars (Pacsu, *loc. cit.*).

The procedure described by Pacsu was followed with exactly similar results with one exception, namely, that, although the yellow addition compound formed by the sugar and titanium tetrachloride displayed an upward mutarotation in both cases, the initial rotation of the glucoside complex was negative whereas Pacsu observed an initially positive value for the fully acetylated derivatives.

The investigation has not been pursued as it is understood (Pacsu, *Ber.*, 1928, **61**, 1508) that a systematic research into the action of titanium tetrachloride on β-glucosides of different types is in progress.

Tetracetyl-β-d-glucosido-glycollic ester.—This substance was prepared as described by Fischer and Helferich (*A.*, 1911, **383**, 81). It had m.p. 82-83° (uncorrected) and $[\alpha]_D^{21°}$–40·1° in ethyl alcohol (c = 2·005). Found: C, 49·5; H, 5·8. $C_{18}H_{26}O_{12}$ requires C, 49·8; H, 6·0). Fischer and Helferich gave m.p. 83-84° (corr.) and $[\alpha]_D^{23°}$–40·2° in ethyl alcohol.

The Action of Titanium Tetrachloride on Tetracetyl-β-d-glucosido-glycollic ester.

(1) A solution of titanium tetrachloride (2·2 gm.: 1 mol) in absolute chloroform (20 c.c.) was added to tetracetyl-β-d-glucosido-glycollic ester (5 gm.: 1 mol) in the same solvent (30 c.c.). The yellow precipitate which first formed dissolved with the evolution of heat giving a yellow solution which was refluxed gently for 2·5 hours; a small quantity of hydrochloric acid was evolved and the colour of the solution changed to a light golden brown. After cooling, the solution was poured into ice-water, both layers becoming colourless after shaking. The chloroform layer was washed once with ice-cold sodium bicarbonate solution (5%) and thrice with ice-water, dried over sodium sulphate and evaporated under diminished pressure; the residue was treated with ether and petroleum ether giving white needles, m.p. 69-71°. Yield 3 gm. or 71% of the theoretical.

An experiment in which 2 molecules of titanium tetrachloride were used gave a 76% yield of the same substance.

After two recrystallisations from ether-petroleum ether the substance had m.p. 71·5-72·5°, mixed m.p. with a specimen of acetochloroglucose prepared by the action of titanium tetrachloride on glucose β-pentacetate 71-72°

and $[\alpha]_D^{22°}+166{\cdot}8$ in chloroform ($c = 2{\cdot}008$). v. Arlt (M., 1901, **22**, 147) gave for acetochloroglucose m.p. 72-74° and $[\alpha]_D^{20°}+165{\cdot}76$ in chloroform ($c = 2$).

The substance (1 gm.) was dissolved in methyl alcohol (10 c.c.) and shaken with "active" silver oxide (1 gm.) for 16 hours. The product (0·7 gm., m.p. 96-98°) obtained after the removal of the silver compounds and the solvent was recrystallised from methyl alcohol. It had m.p. 103-104°, mixed m.p. with tetracetyl-β-methyl glucoside 103-104° and $[\alpha]_D^{23°}-23{\cdot}4°$ in alcohol ($c = 2{\cdot}01$). Hudson and Dale (*J. Amer. Chem. Soc.*, 1915, **37**, 1280) gave $[\alpha]_D-24{\cdot}6°$ in alcohol.

(2) Equimolecular quantities of the reagents were dissolved in absolute chloroform and mixed; the solution was immediately shaken with ice-water and then treated as in (1). After one recrystallisation from alcohol the product had m.p. 80-81°, mixed m.p. with the original glucoside 80-81° and $[\alpha]_D^{23°}-41{\cdot}3°$ in alcohol ($c = 2{\cdot}002$).

(3) A chloroform solution containing tetracetyl-β-d-glucosido-glycollic ester (1·6500 gm.) and titanium tetrachloride (0·7314 gm.) was made up to 20 c.c. with chloroform. The specific rotations were calculated from the weight of glucoside taken ($l = 0{\cdot}5$).

Time (hours)	0·17	1·0	2·0	3·4	6·25	22·75	52·75
$[\alpha]_D^{19-20°}$ ..	−49·2	−33·9	−9·9	+8·25	+36·4	+101·8	+128

Another solution containing the glucoside (1·4500 gm.) and titanium tetrachloride (0·6498 gm.) was made up to 20 c.c. with chloroform ($l = 0{\cdot}5$).

Time (hours)—								
1·75	4·33	30·0	47·0	54·1	141·4	165·5	190·0	213·5
$[\alpha]_D^{19-21°}$—								
−13·5	+22·2	+104·1	129·0	130·1	135·2	134·9	+134·6	134·6

After 213·5 hours 14 c.c. of the solution were treated in the usual manner, yielding 0·8 gm. of a solid m.p. 70-71°. After one recrystallisation from ether-petroleum ether it had m.p. 71-72°, mixed m.p. with acetochloroglucose 70·5-71·5° and $[\alpha]_D^{23°}$+166·5 in chloroform ($c = 2·023$).

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RESEARCHES ON INDOLES.

PART II.*

THE PREPARATION OF SOME DERIVATIVES OF 5:6-DIMETHOXY INDOLE.

By FRANCIS LIONS, B.Sc., Ph.D.,
and MARY JOAN SPRUSON, B.Sc.

(*Read before the Royal Society of New South Wales, June 1, 1932.*)

Kalb, Schweizer, and Schimpf (*Ber.*, 1926, **59**, 1858) and Kalb, Schweizer, Zellner, and Berthold (*ibid.*, p. 1860) seem first to have applied the Japp-Klingemann reaction (*Ber.*, 1888, **21**, 549; *Ann.*, 1888, **247**, 218) to the preparation of the necessary monophenyl hydrazones of α-diketones and α-keto esters for use as intermediates in Fischer's indole synthesis. The method has since been exploited by Manske, Perkin and Robinson (*J.C.S.*, 1927, 2), Manske and Robinson (*ibid.*, p. 240), Jackson and Manske (*J.A.C.S.*, 1930, **52**, 5029), and by Manske (*Can. J. Research*, 1931, **4**, 591-5). Its great value lies in the facts that the reaction almost invariably gives excellent yields of substituted hydrazones, and that a diazotisable aromatic amine forms the starting material

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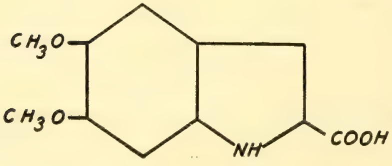
* Part I of this series appeared in the *Journal and Proceedings of the Royal Society of N.S.W.* (1929), LXIII, 168.

rather than the corresponding aryl hydrazine, which may often be extremely difficult to prepare. Certain indole derivatives thus become readily accessible, which would otherwise be almost impossible to obtain.

In the work described in the present communication, the possibility of obtaining various derivatives of 5:6-dimethoxy indole from 4-amino veratrole, utilising the Japp-Klingemann reaction, has been explored with encouraging results. Perkin and Rubenstein (*J.C.S.*, 1927, 357) showed that 3:4-dimethoxy phenyl hydrazine is obtainable only with difficulty, and is exceptionally unstable. With certain ketones it gives the corresponding 3:4-dimethoxy phenyl hydrazones and from these the corresponding 5:6-dimethoxy indoles can be obtained, by cyclisation with alcoholic hydrochloric acid, but the overall yields are extremely bad. The method has, consequently, little to recommend it for preparative work.

Oxford and Raper (*J.C.S.*, 1927, 417) later essayed the preparation of various 5:6-dimethoxy indole derivatives, and eventually prepared 5:6-dimethoxy indole 2-carboxylic acid (I) and 5:6-dimethoxy indole (II) in poor yield from 6-nitro homoveratrole by a modification of Reissert's method. Their process is, however, not available as a general method of synthesis.



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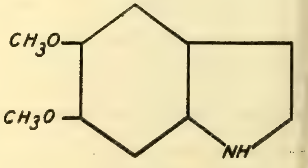
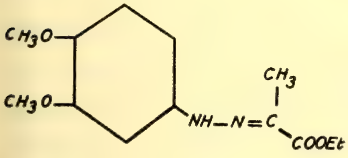


II

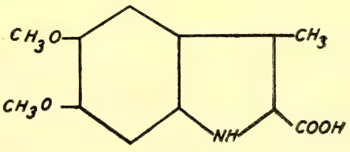
The importance of derivatives of 5:6-dimethoxy indole has been pointed out by Perkin and Rubenstein and by Oxford and Raper (*loc. cit.*); whilst the very interesting possibility that the alkaloid brucine is a derivative of 5:6-dimethoxy dihydro indole [*cf.*, for example, Robinson, Bakerian Lecture, *Proc. Roy. Soc.*, **130**, A.441; Leuchs, Ber., **64**, 462, (1931)] renders necessary a general method for the synthesis of such substances.

Ethyl α-acetyl propionate condenses directly with 3:4-dimethoxy benzene diazonium chloride in alkaline alcoholic solution with elimination of the acetyl group, yielding ethyl pyruvate 3:4-dimethoxy phenyl hydrazone (III) as a dark red oil, in excellent yield. Rapid saturation of an alcoholic solution of this oily hydrazone with dry hydrogen chloride, without cooling, followed by allowing the hot solution to stand for 30 minutes, leads to the precipitation of ammonium chloride and the formation in good yield of the ethyl 5:6-dimethoxy indole-2-carboxylate, M.P. 174° C., previously prepared by Perkin and Rubenstein (*loc. cit.*). Hydrolysis of this ester gives the corresponding acid (I; M.P. 203° C.), previously prepared by Oxford and Raper (*loc. cit.*, p. 421).

In a similar manner 3-methyl 5:6-dimethoxy indole-2-carboxylic acid (IV) and 3-phenyl 5:6-dimethoxy indole-2-carboxylic acid (V) are readily obtained from



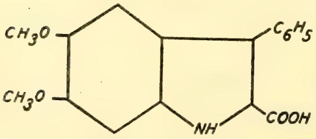
III



IV

ethyl α-acetyl butyrate and ethyl α-acetyl β-phenyl propionate respectively. Coupling of 3:4-dimethoxy benzene diazonium chloride with ethyl cyclohexanone-2-carboxylate in alkaline alcoholic solution gives the 3:4-dimethoxy phenyl hydrazone of the half ester of α-keto pimelic acid (VI) which with dry hydrogen chloride in alcoholic solution is readily cyclised to the corresponding ethyl-γ-(2-carbethoxy 5:6-dimethoxy-3-indolyl)-butyrate (VII), esterification occurring simultaneously.

It is worthy of comment that when any of these hydrazones of α-keto esters is first hydrolysed with alcoholic potash, prior to treatment with alcoholic hydrogen chloride, almost invariably this acid treatment leads to the formation of tarry matter, and the inability to isolate any indole formed. This behaviour is to be attributed to the instability of the 5:6-dimethoxyindole-2-carboxylic acids to mineral acids, as already noted by Oxford and Raper (*loc. cit.*, p. 420). Undoubtedly a procedure similar to that adopted by us should give improved yields in analogous indole cyclisations.



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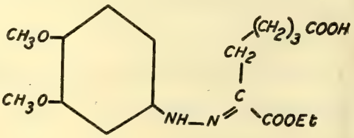
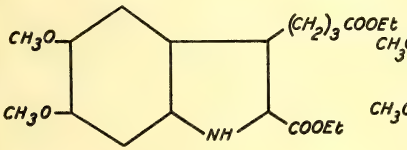


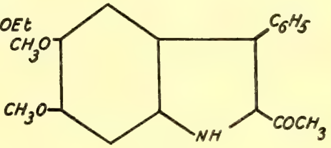
VI

Finally, it has been shown, by an example, that the method is available for the preparation of 5:6-dimethoxy-2-acyl indoles. Coupling of 3:4-dimethoxy benzene diazonium acetate with the sodium salt of α-acetyl-β-phenyl propionic acid occurs readily with the evolution of

carbon dioxide, and the 3:4-dimethoxy phenyl hydrazone of 2:3-diketo-4-phenyl butane is obtained crystalline in almost quantitative yield. This cyclises readily with alcoholic hydrogen chloride to yield the corresponding 2-acetyl-3-phenyl 5:6-dimethoxy indole (VIII).



VII



VIII

Experimental.

Ethyl-5:6-dimethoxyindole-2-carboxylate.

An ice-cold solution of potassium hydroxide (14 g.) in water (30 c.c.) was added to an ice-cold solution of ethyl α-acetyl propionate (15 g.) in alcohol (180 c.c.); then a solution of 3:4-dimethoxy benzene diazonium chloride (from 3:4-dimethoxy aniline hydrochloride [20 g.; *cf.* Fargher, *J.C.S.*, **1920**, 869) in water (30 c.c.) and concentrated hydrochloric acid (40 c.c.)] was added without delay, and the solution kept vigorously stirred. The hydrazone was precipitated as a heavy brown oil. After ten minutes, water (600 c.c.) was added and the oily hydrazone extracted twice with ether. The combined ethereal extracts were thoroughly washed with water, dried with anhydrous sodium sulphate and the solvent removed. Yield 24 g.

A solution of this crude hydrazone (10 g.) in dry alcohol (100 c.c.) was rapidly saturated with dry hydrogen chloride until the alcohol boiled. Ammonium chloride separated and the solution changed colour, from

red brown to green. After standing thirty minutes the solution was cooled, ether (500 c.c.) added and the alcohol and excess of hydrochloric acid washed out with water. After drying and removal of the solvent, ethyl-5:6-dimethoxyindole-2-carboxylate (6 g.) remained as an oil which was induced to crystallise. It was recrystallised from ethyl alcohol, in which it is readily soluble in the hot, and obtained in orange yellow needles. M.P. 174° C. Perkin and Rubenstein (*J.C.S.*, 1927, 360) give the M.P. as 172° C.

5:6-Dimethoxyindole-2-carboxylic acid (I).

This substance was obtained by the hydrolysis of this ester with alcoholic potash, followed by removal of the alcohol and acidification with dilute hydrochloric acid. It was recrystallised from hot water and thus obtained in fine white matted needles. M.P. 203° C. (Oxford and Raper, *loc. cit.*, give the M.P. as 202-203° C.).

Ethyl-3-methyl-5:6-dimethoxyindole-2-carboxylate.

Ethyl α-keto butyrate 3:4-dimethoxy phenyl hydrazone was obtained as described above by coupling ethyl α-acetyl butyrate (17 g.) in alcohol (180 c.c.) and sodium hydroxide (14 g.) in water (30 c.c.) with 3:4-dimethoxy benzene diazonium chloride [from 3:4-dimethoxy aniline hydrochloride (20 g.) in water (30 c.c.) and concentrated hydrochloric acid (40 c.c.)]. A red brown oil (25 g.) was obtained. This crude hydrazone was converted to the corresponding indole by treatment with alcoholic hydrogen chloride as before, and the resulting liquid was poured into water. The precipitated oil soon solidified and was recrystallized first from methyl and then from

ethyl alcohol, and obtained as orange needles, M.P. 182° C.

(Calcd. for $C_{14}H_{17}O_4N$, C = 63·8, H = 6·5%. Found C = 64·4, H = 6·5%.)

3-Methyl-5:6-dimethoxyindole-2-carboxylic acid (IV).

This substance was obtained by hydrolysis of the above ester with alcoholic potassium hydroxide. Recrystallized from ethyl alcohol, it was obtained in pale pink needles, the mother liquor being green. M.P. 208° C. (decomp.). Alcoholic solutions of these indole carboxylic acids were usually deep purple in shade.

(Calcd. for $C_{12}H_{13}O_4N$, C = 61·4, H = 5·5%. Found C = 61·6, H = 5·9%.)

Ethyl-3-phenyl-5:6-dimethoxyindole-2-carboxylate.

Ethyl-β-phenyl pyruvate 3:4-dimethoxy phenyl hydrazone was obtained as described above by coupling ethyl α-acetyl-β-phenyl propionate (22 g.) in alcohol (180 c.c.) and sodium hydroxide (13 g.) in water (30 c.c.) with 3:4-dimethoxy benzene diazonium chloride [from 3:4-dimethoxy aniline hydrochloride (20 g.) in water (30 c.c.) and concentrated hydrochloric acid (40 c.c.)].

The hydrazone separated as a dark red oil. Yield 34 g. The whole was converted to the corresponding indole by treatment with alcoholic hydrogen chloride as before, but, in addition, the solution was heated for fifteen minutes before pouring into water. The brown solid was recrystallised from ethyl alcohol and thus obtained in pale orange platelets, in good yield, M.P. 167° C.

(Calcd. for $C_{19}H_{19}O_4N$, C = 70·2, H = 5·9%. Found C = 69·8, H = 6·0%.)

3-Phenyl-5:6-dimethoxyindole-2-carboxylic acid (V)

This substance was obtained by hydrolysis of the above ester. After addition of water, and removal of alcohol, the alkaline solution was boiled with animal charcoal, and filtered before acidification. The solid acid recrystallised from alcohol in fine white matted needles. M.P. 203° C. (decomp.).

(Calcd. for $C_{17}H_{15}O_4N$, C = 68·7, H = 5·0%. Found C = 69·0, H = 4·8%.)

Ethyl-(-2-carbethoxy-5:6-dimethoxy-3-indolyl)-butyrate (VII).

The 3:4-dimethoxy phenyl hydrazone of the half ester of α-keto pimelic acid was obtained as described above by the coupling of ethyl cyclohexanone-2-carboxylate (15·5 g.) in alcohol (180 c.c.) and sodium hydroxide (12 g.) in water (30 c.c.), with 3:4-dimethoxy benzene diazonium chloride [from 3:4-dimethoxy aniline hydrochloride (17·5 g.) in water (30 c.c.) and concentrated hydrochloric acid (40 c.c.)]. A very dark brown oil separated, which was taken up and dried in ether. Yield 30 g.

This hydrazone (20 g.) was converted to the corresponding indole by treatment with dry hydrogen chloride, in the usual way. Ether was then added to the alcoholic solution and the alcohol and excess acid washed out. After drying and removal of the ether, the still liquid substance soon solidified. It was purified by distillation at low pressure. B.P. 272°-274°/0·7 mm. Yield 10·6 g.

The distillate was recrystallised from ether, and obtained in fluffy aggregates of a creamy colour; M.P. 163° C.

No crystallisable substance was obtained on hydrolysis of this substance, which proved to be the di-ethyl ester.

(Calcd. for $C_{19}H_{25}O_6N$, C = 62·8, H = 6·9%. Found C = 62·5, H = 6·8%.)

2-Acetyl-3-phenyl-5:6-dimethoxyindole (VIII).

Sodium hydroxide (4 g.) in water (10 c.c.) was added to ethyl α-acetyl β-phenyl propionate (17 g.) in alcohol (20 c.c.) until a jelly was formed. Water (200 c.c.) was added and the whole was stirred until only a little jelly remained unacted upon (*cf.* Manske, Perkin and Robinson, *J.C.S.*, 1927, 9). This was removed by passing through a wet filter paper. To this was added a solution of 3:4-dimethoxy benzene diazonium chloride [from 3:4-dimethoxy aniline hydrochloride (16·5 g.) in water (20 c.c.) and concentrated hydrochloric acid (15 c.c.)]. The liberation of carbon dioxide caused by the addition of sodium acetate (40 g.) caused the mono veratryl hydrazone of 2:3-diketo-4-phenyl butane to rise to the top of the solution. The hydrazone solidified on standing, and was filtered off. Yield nearly theoretical. It was recrystallised from alcohol in shining golden plates. M.P. 173° C.

(Calcd. for $C_{18}H_{20}O_3N_2$, C = 69·3, H = 6·4%. Found C = 69·1, H = 6·4%.)

The substance was difficultly soluble in hot alcohol.

About 15 g. of the hydrazone was suspended in alcohol (250 c.c.), to which a little ether had been added. Hydrogen chloride was passed into the solution, which turned green, and ammonium chloride separated after a few minutes heating on the water bath. Ether was added to the cooled solution and the alcohol and ammonium

chloride washed out. After drying and removal of the ether the indole crystallised in pale brown needles, which were recrystallised from alcohol. M.P. 181° C.

(Calcd. for $C_{18}H_{17}O_3N$, C = 73·2, H = 5·8%. Found C = 73·6, H = 6·0%.)

Department of Organic Chemistry,
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FINAL PART OF VOL. LXVI.
ISSUED MARCH 31, 1933.

VOL. LXVI. **PART II.**

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(Plates II–XI.)

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CONTENTS.

VOLUME LXVI.

Part II.*

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THE OCCURRENCE OF A NUMBER OF VARIETIES OF *EUCALYPTUS RADIATA* (*E. NUMEROSA*) AS DETERMINED BY CHEMICAL ANALYSES OF THE ESSENTIAL OILS.

PART I.

By A. R. PENFOLD, F.A.C.I., F.C.S.,
Curator and Economic Chemist;

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(*Read before the Royal Society of New South Wales, July 6, 1932.*)

Since the publication of our paper entitled "The occurrence of a number of varieties of *Eucalyptus dives* as determined by chemical analyses of the essential oils—Part I", read before this Society on 1st June, 1927 (see *Jour. and Proc. Roy. Soc. N.S.W.*, lxi, 54-67), we have made similar observations on *Eucalyptus piperita, E. hœmastoma, E. phellandra, E. radiata* and *Melaleuca leucadendron.* The examination of many samples of material from numerous districts and, in some instances, different States of the Commonwealth, occupies considerable time and, consequently, the summarising of the results must be deferred for the present. We are, however, in a position to make available the results of a field investigation, supported by the examination of the essential oils of *Eucalyptus radiata.*

The investigation was confined to one locality, *viz.*, Nullica, a small village on the Prince's Highway, about six miles from Eden, New South Wales. The influence of the results on the economic exploitation of this species warrants an early publication of the results in a Part I communication.

Eucalyptus radiata, sometimes called *Eucalyptus numerosa* (Maiden, *Proc. Roy. Soc. N.S.W.*, li, 461), is a fairly tall tree, known vernacularly as River White Gum. It is found widely distributed on the river banks, but preferably creeks, and mountain ranges of the coast districts of New South Wales, and is particularly abundant in the southern areas. The chemistry of the essential oils of the type is fully described in "Eucalypts and Their Essential Oils", by Messrs. Baker and Smith (Second Edition, 1920), page 306, and by A. R. Penfold in Bulletin No. 2 (Revised Edition), page 14, issued by the Sydney Technological Museum. Until the observations to be described were made, the essential oil of this species was found to be of a remarkably uniform chemical composition, consisting principally of phellandrene (70% to 80%) with piperitol. The content of piperitone did not exceed 5%. The alcohol, piperitol, was first isolated from this oil, which contains it to a greater extent than any other Eucalyptus oil as yet described.

The receipt of a bag of leaves of this species from Mr. S. Havard, of Nullica, *via* Eden, New South Wales, in June, 1930, for a report as to the value of the essential oil, led to a unique observation. Morphologically, *Eucalyptus radiata* is comparatively easy to identify, although we have observed instances of its confusion with *Eucalyptus Australiana* (Baker and Smith, *Proc.*

Roy. Soc. N.S.W., 1915, p. 514). The leaves and terminal branchlets submitted were definitely identified as *E. radiata* and on crushing the leaves between the fingers it was observed that some possessed the characteristic odour of piperitol by which the species is easily distinguishable from other "narrow-leafed peppermints", whilst others had a more pronounced peppermint odour typical of *E. dives* rich in piperitone. An attempt was made to separate as well as possible what appeared to be two different forms by the tedious and difficult procedure of crushing the leaves of the various terminal branchlets and observing the odour. Time and patience did not permit of the total quantity being handled in this manner, but the results of the examination of the essential oils of the two different forms thus separated, as well as the remainder of the mixed leaves as received, confirmed in a surprising manner the excellence of the separation, as well as the identity of a physiological form of *E. radiata*. The results as set forth in Table "A" show that an essential oil practically equivalent in general physical and chemical characters to that obtained from *E. dives* is obtained from this new form (piperitone 50%, phellandrene 40%). This observation is of considerable importance, for, whilst there is little or no enquiry at present for the oil of *E. radiata* as represented by the type (5% piperitone), there is always a demand for oils rich in piperitone. We are not unmindful, of course, of the difficulty which cutters would experience in their endeavours to distinguish the two forms, but, nevertheless, there is always the possibility of a belt of a particular form being observed (see *Jour. Proc. Roy. Soc. N.S.W.*, lxiii, 83-84).

TABLE "A."

Eucalyptus radiata.

Date.	Weight of Leaves.	Yield of Oil.	$d\frac{15}{15}°$	$a_D^{20°}$	$n_D^{20°}$	Solubility in 70% Alcohol.	Piperitone Content.	Cineol.	Phellandrene.	Remarks.
	lbs.	%				Vols.	%			
12/6/1930.	8½	2·7	0·9010	−59·5°	1·4795	1·3	46	Nil.	Abundance.	Leaves consisted principally of variety "A."
,,	26	2·3	0·8866	−36·25°	1·4770	0·6 (80%)	5	,,	,,	Leaves consisted principally of Type.
,,	8	2·4	0·8926	−39·5°	1·4770	1·5	16	,,	,,	Mixed leaves, as received.

The above results represent the sorting of one bag of leaves and terminal branchlets as received from Mr. S. H. Havard of Nullica, *via* Eden, N.S.W.

A field investigation was undertaken by one of us (A.R.P.) early in November, 1931, in order to secure confirmation of the above-mentioned observations. Many trees were individually examined in the presence of Mr. B. Pigott, the Forester at Eden, New South Wales, and until they were felled and the leaves examined it was impossible to distinguish one tree from another. A number of trees were selected, some of which were growing within a few feet of each other, whilst others were situated some distance apart, but all within a definite area of several acres. The leaves were duly crushed and the odours noted. A small quantity of leaves was taken from a number of specially selected trees and brought to Sydney for distillation. The results are set forth in Table "B" and in every instance the field observations were confirmed. The leaves of one particular tree, marked No. 1 in Table "B", were found to give a pronounced odour of cineol in the field. The amount actually determined appears to be less than the field observation led one to believe, but, nevertheless, the identification of this constituent is of special interest as its occurrence in the oil of *E. radiata* has not hitherto been recorded.

It was our intention to examine the sucker growth on the stumps of the trees from which the original consignment of leaves received in June, 1930, was obtained. Unfortunately, certain circumstances prevented this observation. Subsequently arrangements were made by correspondence for collections of the sucker leaves to be secured and forwarded for examination. The results are set forth in Table "C", and as the foliage from each individual tree was kept separate, abundant evidence in

TABLE "B."
Eucalyptus radiata.

Date and Lot No.	Weight of Leaves.	Yield of Oil.	$d\frac{15°}{15°}$	$a_D^{20°}$	$n_D^{20°}$	Solubility in 70% Alcohol.	Piperitone Content.	Cineol Content.	Phellandrene.	Ester No. 1½ hrs. Hot Sap.	Ester No. after Acetylation.	Remarks.
11/11/1931 No. 1	lbs. 5¾	% 2·7	0·9034	−42·1°	1·4737	Vols. 1·4	% 22	About 12 to 15%	Abundance	46·1	101·2	Leaves from a large tree with cineol odour.
No. 2	2	1·7	0·9009	−40·2°	1·4740	1·2	28	About 12 to 15%	Abundance	58·2	—	Sucker leaves from base of tree No. 1.
No. 3	2¾	2·9	0·9047	−59·2°	1·4816	1·2	52	Nil.	Abundance	60·9	89·4	Leaves from small tree with piperitone odour.
No. 4	4¾	2·3	0·8945	−38·7°	1·4779	1·3	6	Nil.	Abundance	33·6	78·9	Leaves from small tree with piperitol odour.
No. 5	2½	2·3	0·9054	−32·4°	1·4809	1·2	12	Nil.	Moderate quantity.	58·8	—	Leaves from small tree with piperitol odour.
No. 6	8¾	3·1	0·9029	−64·7°	1·4808	1·3	52	Nil.	Abundance	90·9	86·9	Leaves from small tree with piperitone odour.
No. 7	1½	2·5	0·9051	−32·25°	1·4800	1·1	18	Nil.	Moderate quantity.	64·3	—	Leaves from small tree with piperitol odour.

Leaves collected by Mr. A. R. Penfold, at Nullica, *via* Eden, N.S.W.
Nos. 4 and 5 are typical of *Eucalyptus radiata* (Type).
Nos. 3 and 6 are typical of *Eucalyptus dives* and therefore represent a variety of *E. radiata* to be called variety "A."
Nos. 1 and 2 are representative of another variety to be called variety "B."
No. 7 is most probably an intermediate form.

support of our contention that the original consignment of foliage was from mixed leaves was thus obtained.

As a result of our investigations, we are of the opinion that several distinct varieties of *E. radiata* exist. This species, therefore, exhibits similar behaviour to that of *E. dives,* and doubtlessly further investigations will reveal the fact that the existence of these physiological forms is common to a large number of Eucalypts. The forms observed at Nullica, *via* Eden, are as follows:

E. radiata—Type: Essential oil contains piperitone, 5-10%; phellandrene, 60-80%; with piperitol.

E. radiata—Var. A: Essential oil contains piperitone, 50%; phellandrene, 40%.

E. radiata—Var. B: Essential oil contains piperitone, 20-30%; cineol, 12-15%; phellandrene, 40%, and piperitol.

The variety "A" would be of considerable economic importance if a stand or area of the trees, comparatively free of the type, could be located.

Our thanks are due to Mr. Frank Kelly, Nullica, N.S.W., for kindly collecting the supplies of leaves referred to in Table "C", and particularly to Mr. B. Pigott, Forester at Eden, for arranging the transport of the various collections, as well as his action in placing his services at our disposal during the field inspection.

Experimental.

The various collections of leaves and terminal branchlets, cut as for commercial purposes, were subjected to steam distillation in the usual manner. The chemical and physical characters of these various distillates are set forth in Tables "A", "B" and "C".

TABLE "C."

Eucalyptus radiata.

Date and Lot No.	Weight of Leaves.	Yield of Oil.	$d\frac{15}{15}°$	$a_D^{20°}$	$n_D^{20°}$	Solubility in 70% Alcohol.	Piperitone Content.	Cineol Content.	Phellandrene.	Ester No. 1½ hours Hot Sap.	Ester No. after Acetylation.	Remarks.
30/11/1931 No. 1	lbs. 3¾	% 2·2	0·9039	−45·5°	1·4811	Vols. 1·2	% 45	Nil.	Abundance	92·7	194·1	Leaves from original stump. 12/6/1930.
No. 1A	12	2·9	0·8808	−41·2°	1·4784	10·0	6	Nil.	Abundance	19·9	56·6	Leaves from tree alongside original stump. 12/6/1930.
No. 2	19¼	2·3	0·8764	−37·4°	1·4790	Insoluble 10·0 Soluble 0·7 80% Alcohol.	5	Nil.	Abundance	13·0	63·3	Leaves from tree alongside original stump. 12/6/1930.
No. 3	19	2·7	0·9036	−63·2°	1·4809	1·3	55	Nil.	Abundance	65·1	146·3	Leaves from original stump. 12/6/1930.

Leaves collected by Mr. F. Kelly, Nullica, N.S.W., from original trees referred to in Table "A."

A very sharp line of demarcation is provided in the chemical composition of the oils from the type and variety "A".

Although the chemical composition of the essential oils of most of the Eucalypts is well known, particularly those of *E. dives* and *E. radiata,* it was deemed advisable to definitely identify the principal constituents.

EUCALYPTUS RADIATA, TYPE.

The essential oils of this species varied from almost water white to pale straw yellow in colour, and possessed a distinctive odour of piperitol which readily distinguishes it from most other species. The constituents, so far identified, are *l*-α-phellandrene 60-80%, piperitone usually 5%, with the alcohol piperitol.

The phellandrene differed slightly in its physical characters from that obtained from variety "A", and we are of the opinion that the oil of this species would repay more critical examination. We propose to undertake this work at a suitable opportunity.

Oils obtained from lots 1[a] and 2 of 30th November, 1931, were subjected to fractional distillation and detailed examination.

Lot 1[a], 30.11.31.

100 cc. crude oil gave the following results on distillation, *viz.,* first drops 55° (11 mm.).

Fraction.	Volume.	$d^{15^\circ}_{15}$	$a^{20^\circ}_{D}$	$n^{20^\circ}_{D}$
55°–75° (11 mm.) ..	65 cc.	0·8588	−48·4°	1·4781
75°–100° (11 mm.) ..	27 cc.	0·9194	−29·6°	1·4775
Residue	7 cc.			1·4792

Lot No. 2, 30.11.31.

100 cc. crude oil gave the following results on distillation, *viz.*, first drops 40° (14 mm.).

Fraction.	Volume.	$d_{15°}^{15°}$	$a_D^{20°}$	$n_D^{20°}$
Below 67° (10 mm.)	29 cc.	0·8517	−43·2°	1·4792
Below 75° (10 mm.)	40 cc.	0·8587	−41·0°	1·4803
75° (10 mm.)–95° (6 mm.)	25 cc.	0·9516	−29·0°	1·4778
Residue	5 cc.			1·4963

Determination of l-a-phellandrene.

The terpene fractions from Nos. 1[a] and 2 were mixed together, fractionally distilled, and finally redistilled several times over metallic sodium, when the following results were obtained, *viz.*:

Fraction.	Volume.	$d_{15°}^{15°}$	$a_D^{20°}$	$n_D^{20°}$
Below 70° (20 mm.)	16 cc.	0·8484	−43·2°	1·4774
70°–71° (20 mm.) ..	48 cc.	0·8473	−48·7°	1·4770
71°–75° (20 mm.) ..	58 cc.	0·8492	−48·75°	1·4702

No other terpene or hydrocarbon could be detected beyond phellandrene. The oil yielded the characteristic nitrosite melting at 113° which after rigorous purification rose to 121°-122°. The specific rotation in chloroform was found to be +137·2.

Determination of Piperitol.

Those portions of lots Nos. 1[a] and 2 boiling above the terpene fractions were mixed together and redistilled, when the following fractions resulted:

Fraction.	Volume.	$d\frac{15°}{15}$	$a_D^{20°}$	$n_D^{20°}$
75°–89° (10 mm.) ..	9 cc.	0·8934	−25°	1·4780
90°–101° (10 mm.) .. (94°–98°)	42 cc.	0·9223	−30°	1·4768

A portion of the second fraction after removal of associated piperitone by means of neutral sodium sulphite solution was oxidised with Beckman's chromic acid mixture, and the piperitone prepared therefrom purified through the bisulphite compound using sodium sulphite. The piperitone was identified by the preparation of the β semicarbazone melting at 175°-176°.

EUCALYPTUS RADIATA, VARIETY "A".

The oils of this variety varied from almost water white to a pale straw yellow in colour, and possessed the characteristic odour of piperitone. The constituents, so far identified, are *l*-α-phellandrene, about 40%, and *l*-piperitone, 50%.

In chemical and physical characters the oil is practically indistinguishable from that of *E. dives.*

The oil obtained from sample marked "Lot No. 3" in Table "C" was submitted to fractional distillation, and its principal components definitely determined.

Lot No. 3, 30.11.31.

80 cc. crude oil gave the following results on distillation, *viz.*:

Fraction.	Volume.	$d_{15°}^{15}$	$a_D^{20°}$	$n_D^{20°}$
70°–90° (20 mm.) ..	30 cc.	0·8569	−80·4°	1·4799
90° (20 mm.)–118° (16 mm)	49 cc.	0·9300	−52·2°	1·4841
Residue				1·4979

Determination of l-a-phellandrene.

The fraction distilling at 70°-90° (20 mm.) was redistilled several times over metallic sodium, when the following final distillate was obtained, *viz.*: Boiling point 91° (60 mm.) $d_{15°}^{15}$ 0·8456, $a_D^{20°}$ −85°·2, $n_D^{20°}$ 1·4728. The nitrosite melted at 121°–122°.

The terpene obtained from this lot differed considerably in its physical characters from that obtained from lots Nos. 1[a] and 2. It was identical with 1-a-phellandrene prepared from the oil of *Eucalyptus dives.*

Determination of Piperitone in Sample of Oil No. 3.

A fraction of boiling point 91° (20 mm.)–118° (16 mm.) was treated with neutral sulphite solution when 27 cc. of purified ketone was returned. This sample had boiling point 108°·5–110° (9–10 mm.), $d_{15°}^{15}$ 0·9379, $a_D^{20°}$ −1·5°, $n_D^{20°}$ 1·4842. Unfortunately the sodium sulphite used was of poor quality and the regenerated ketone had lost much of its original laevo-rotation. It was treated with excess of hydroxylamine when the characteristic

α-oxime melting point 118°–119° was obtained, together with the hydroxylamino-oxime of which two fractions were obtained of melting point 169°–170° and 180° respectively. Confirmation of the presence of laevo-rotatory piperitone was obtained by working up 60 cc. of the crude oil of lot No. 1 in Table "A" which yielded on distillation 30 cc. of oil boiling between 90° and 111° (10 mm.). This sample on treatment with neutral sodium sulphite solution and regeneration with sodium hydroxide solution returned 18 cc. of the purified ketone. The oil possessed the following chemical and physical constants, *viz.*: Boiling point 109°–110° (10 mm.), $d_{15°}^{15}$ 0·9377, $a_D^{20°}$ −38°·6, $n_D^{20°}$ 1·4843.

The hydroxylamino-oxime prepared therefrom was separated into two fractions melting at 169°-170° and 180° respectively.

EUCALYPTUS RADIATA, VARIETY "B".

This variety yields an essential oil very similar in physical characters to those obtained from the Type and Variety "A". The principal constituents which have so far been identified are *l*-α-phellandrene, piperitone 22-30%, cineol 12-15%, together with piperitol.

The cineol content was accurately determined by the ortho-cresol method utilising that portion of the oil distilling below 190° (764 mm.).

THE INTRUSIVE IGNEOUS ROCKS OF THE MUSWELLBROOK-SINGLETON DISTRICT.

PART II.

THE SAVOY SILL.*

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With Rock Analyses by

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(With Plates II, III and IV, and four text-figures.)

(Read before the Royal Society of New South Wales, July 6, 1932.)

Part I of this paper was read before the Society on June 4, 1930, and consisted of an introduction to a detailed study of the intrusive igneous rocks of the Muswellbrook-Singleton coalfield. In the introductory statement concerning these rocks, it was pointed out that[1] "the field examination . . . . and a preliminary investigation of their petrology indicate that they fall into three groups as follow:

1. Alkaline basic sills.
2. Plugs.
3. Dykes and small sills." (Basalt.)

The alkaline basic sills are those which occur at Savoy, Plashett, Carrington and Fordwich. Their distribution is

* Published with the permission of the Under-Secretary for Mines.

shown in Plate IV of the earlier communication, and all except the last-named are shown in Fig. 1 of this paper. The Savoy mass differs from the other sills by its much higher proportion of acid rocks, which in places contain quartz, a mineral not known to be present in the rocks from the other sills. It also presents some interesting departures from the sill form in its mode of occurrence. It is considered, therefore, that a separate communication giving a detailed account of the geology and petrology of the Savoy Sill is well warranted.

In the following pages the field and general geology is the work of H. G. Raggatt, and the petrology of H. F. Whitworth. There has, however, been free interchange of ideas, and each has criticised the work of the other. The rock analyses are the work of W. A. Greig.

Topography.

Locality and Means of Access.

The intrusion which forms the subject of this paper occurs eight miles southerly from Muswellbrook and is mainly within the Parish of Savoy, County of Durham. The outcrop extends also into the Parish of Wynn, the Savoy trigonometrical station being on the boundary between the two parishes. The area is part of the "Edinglassie" holding.

The only convenient means of access is by an unsurveyed track which leaves the Muswellbrook-Denman road at the same point as the Wollombi stock route, about the middle of the south boundary of portion 3, Parish of Brougham. The track is unfenced, but well defined as far as Saddler's Creek. The stock route itself cannot be

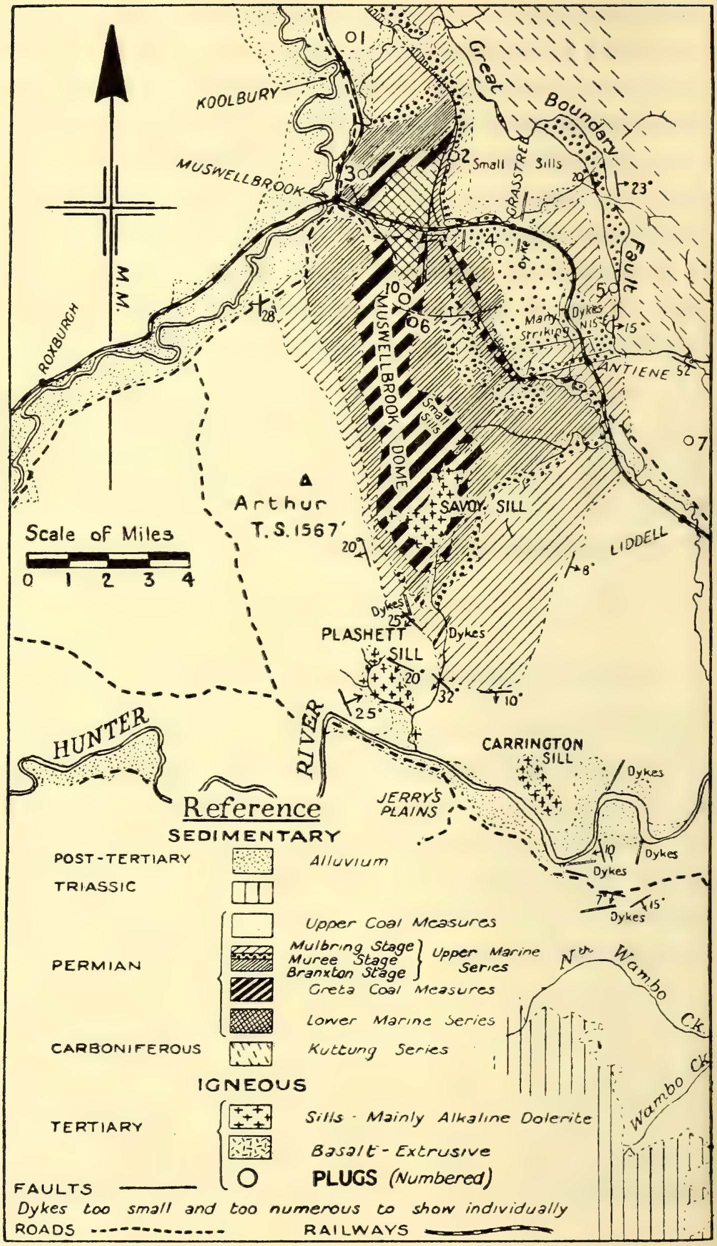

Fig. 1.—Geological Map of part of the Muswellbrook-Singleton district, showing distribution of igneous rocks.

travelled by motor car, but is a useful traversed line for survey purposes.

Physiography.

The topography is related to the geological structure (see Plate II and Fig 1). The Savoy trigonometrical station, which is 1,047 feet above sea level, is situated on a well-defined divide developed approximately along the longer axis of the Muswellbrook dome. Beginning at the north boundary of the map (Plate II), the top of this divide is a gently cruved line convex to the east. It is defined at the north end of the map by the stock route which follows it to the north-western corner of the area occupied by igneous rocks. Thence the divide curves gradually to the south-west through Savoy hill, an acid type of igneous rock forming the top of the ridge. The divide separates the waters of Saddler's and Pringle's Creeks, which are strike streams. The creeks in the north-east quarter of the map are, on the whole, dip streams.

Easterly from the Savoy ridge the hills extend for a considerable distance at the same general level of about 800 feet, the amount of relief being from 150 to 200 feet. On the western side of the Savoy ridge the country rises steeply from Saddler's Creek to a high divide which extends nearly to the Hunter River at Denman. This divide is being cut into from the north by the Upper Hunter River and from the south by the Lower Hunter. Its highest points are Mt. Arthur (1,567 feet) and Mt. Ogilvie (1,518 feet), the only hills within the broad valley of the Hunter which are at all comparable in height with the level (2,000 feet) of the uplifted peneplain out of which the valley is carved.

Southwards there is a gradual fall to the Hunter River six miles away. Beyond this the country rises gradually for approximately four miles to the foot of the Broke-Denman escarpment which borders a plateau (the uplifted peneplain referred to above) with a general level of about 2,000 feet.

Field Relations and General Geology.

As the map (Fig. 1) shows, the Savoy intrusion is situated at the southern end of the Muswellbrook dome. This structure is developed in beds of Kamilaroi (Permian) age. It is asymmetric, the dip on the east and south being from five to eight degrees, and on the west twenty degrees. The intrusion is wholly confined (at its outcrop) to the Greta Coal Measures and is developed mainly on the eastern side of the meridional axis of the dome.

Apart from a well-marked modification of the plan of the outcrop westerly from the Savoy hill, the area occupied by igneous rocks is roughly rectangular in shape, the longer sides being arranged in a direction N. 20° E. (*i.e.,* parallel to strike of the sediments on the eastern limb of the Muswellbrook structure). It is three miles long, and has an average width of slightly more than half a mile. Actual exposures occupy somewhat less than two and a quarter square miles.

Rock Types, Outcrops and Weathering.

In the field three distinct types of igneous rock may be recognised: *dolerite, syenite* and *basalt,* the first-named being by far the most abundant. This is not apparent upon casual inspection, as weathering of the dolerite

produces a black soil, whilst the syenite is relatively little decomposed, and appears as fragments scattered through the black soil.

The principal outcrops of *dolerite* are: in the bed of Pringle's Creek and its eastern headwater tributary; along the upper contact parallel to Pringle's Creek; along the lower contact north from the shaft near the Savoy T.S., and in a small creek about three-quarters of a mile south-westerly from the trigonometrical station. There is in fact a general tendency for the dolerite to form fairly good outcrops along the margins of the sill as now exposed, and in the creek beds, and to be represented elsewhere by a deep mantle of black soil. The marginal arrangement of the occurrences suggests the development of a chilled marginal phase, more resistant to erosion than the remainder of the mass. Most of these outcrops are on relatively steep slopes and the products of decomposition are removed as they are formed. This is certainly the explanation of the stream bed outcrops. Pringle's Creek and its eastern headwater tributary are perennially flowing streams which also are able periodically to scour their beds and thus expose relatively fresh areas of dolerite. The tributaries which join Pringle's Creek on the western side, however, rarely flow, and weathering has proceeded to depths of ten feet or more, giving a rich black soil. (For this reason Pringle's paddock is regarded as one of the best in the Muswellbrook district for stock flattening purposes.) It is suggested later (p. 217) that the softening of the rock is due to magmatic processes rather than to the ordinary processes of weathering, but the above-mentioned factors have no doubt been important.

The weathering of the dolerite has also led to the formation of small local deposits of sands with a heavy mineral concentrate consisting largely of ilmenite.

The principal outcrops of the *syenite* are those which form the Savoy hill and the prominent hill westerly therefrom. There is also a fairly large outcrop half a mile north-east from the trigonometrical station, two small outcrops three-quarters of a mile northerly from the foregoing and another, half a mile south-east of the station. It will be seen by reference to the map that the principal outcrops of syenite occur on the top of a ridge. Their presence has in fact largely determined the position of the divide between Pringle's and Saddler's Creeks.

The syenite westerly from the trigonometrical station has quite a steep scarp on its western side with a well-marked bench towards the top. The upper surface slopes down gently to the south-east. Towards the top of the hill the rock becomes markedly drusy, many of the cavities being filled with chalcedony.

The *basalt* outcrops mainly as a selvage to the dolerite at the upper contact and as dykes and sills in the adjacent sediments. It is not known to occur at the lower contact. There are some well-defined outcrops on the stock route, and here and there on the Savoy ridge, suggesting that it originally formed a continuous sheet over the top of most of the dolerite.

Reference might be made here to a sill of basalt which occurs three-quarters of a mile north from the most northerly outcrop of dolerite. It is an almost perfect example of the relationship of outcrop to contour. The following section was measured in the bank of a large dam in portion 83, Parish of Savoy.

Generally this sill keeps to the lower of the two horizons shown and is thus in the same stratigraphical position as the Savoy intrusion (see p. 198).

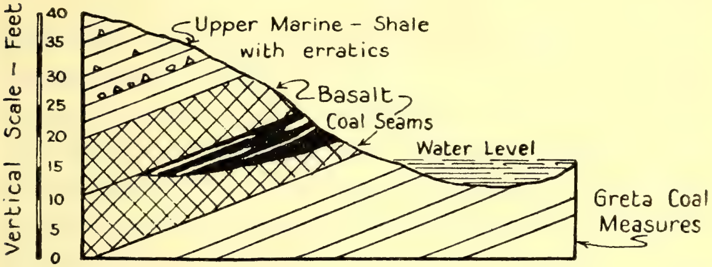

Fig. 2.—Section of a basalt sill exposed in the bank of a dam, portion 83, Parish of Savoy.

Field Relationships between the Rock Types.

The relationship between the dolerite and the syenite is clearly shown in the exposures along Pringle's Creek. In the low cliffs forming the bank of the creek, the syenite is shown to occur as veins and sheets in the dolerite, generally not more than three or four inches thick, but in places up to about ten inches thick. The most common form of occurrence in these sections is irregular sheets approximately parallel to the plane of bedding of the sediments, but there are also numerous small veins with no definite orientation. These types of occurrence are illustrated in Fig. 2 of Plate III.*

The tendency for aplitic veins to take on a stratiform arrangement parallel to the roof and floor of intrusive masses has been noted by many writers. It is a striking feature at Prospect, New South Wales,(2) and has been described by Tyrrell for the Howford Bridge sill, Scot-

* The syenite shown on the Section DE may be a residual of one of these veins or of the roof syenite.

land,(3) and by Ichimura for alkaline intrusives in Korea.(4) The latter also refers to similar occurrences in California which have been described by Taliaferro (so far published in abstract form only apparently).(5)

In the bed of Pringle's Creek there are some good examples of the occurrence of syenite in narrow, sharply bounded veins in the dolerite. The field sketch reproduced in Text-figure 3 shows two principal directions of jointing in the dolerite, N. 35° W. and E. 5° N. The principal syenite veins are from two to three inches wide and are sharply delimited by joint surfaces. Others outcrop merely as threads or "stringers".

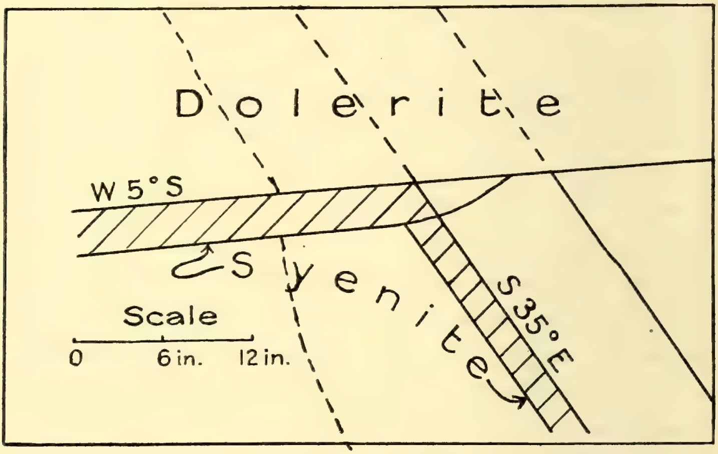

Fig. 3.—Plan showing soda syenite dykes filling joints in analcite dolerite, exposed in the bed of Pringle's Creek. Joints shown by full lines and thin aplitic veins by broken lines. The bearings are strike directions.

The joint directions are approximately parallel to the strike lines of the basalt dykes and to the dominant structure lines of the region.

At the head of a small creek three-quarters of a mile south-west from Savoy T.S., the relationship between the main mass of syenite and the dolerite is well shown, the dolerite forming the south-eastern bank and the syenite the north-eastern. The contact is sharp and may be traced for some distance down the creek, showing that, locally at least, there is an approximately vertical plane of junction between the two types. The syenite forming the hilltops, however, rests upon the dolerite, and the upper surface at least is disposed parallel to the dip of the sediments (Fig. 1 of Plate III and sections, Fig. 4).

There is no conclusive field evidence at the Savoy sill itself as to the age relations between the basalt and the other types of igneous rock. The contact between the two is not well exposed, but there does not appear to be any evidence of gradation between them, and it is doubtful if the basalt can be regarded as a chilled marginal phase of the dolerite. It may be a separate intrusion of related age, since, as already described, it forms a sill on the same horizon as the dolerite a short distance to the north. Evidence of contact effects at the upper surface of the basal precludes the possibility of their being flows.

Form, Limits and Thickness.

That the igneous rocks are intrusive is shown by the contact effects upon the overlying and underlying sediments. The carbonaceous shales are indurated and the overlying coal seam cindered, but these effects are limited to within a few feet of the intrusion. Nevertheless, a very large area of coal has probably been destroyed by this agency.

The top of the sill is about fifteen feet below the top of the Greta Coal Measures, which is well defined in this

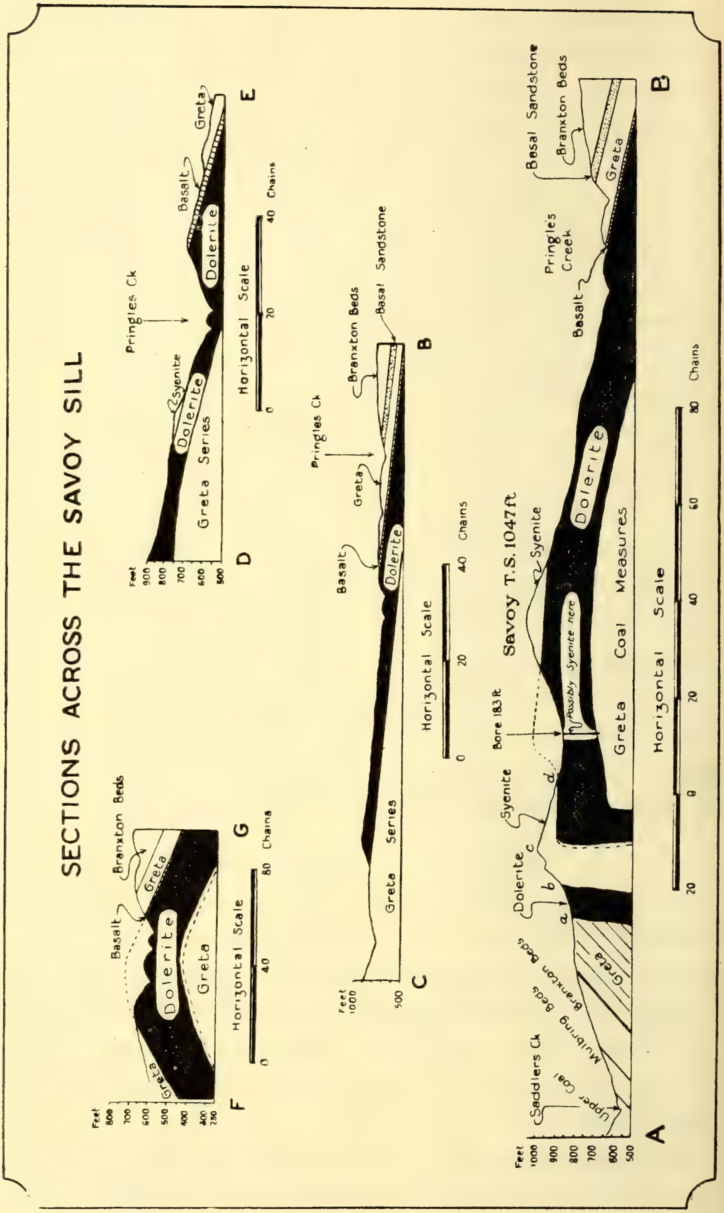
SECTIONS ACROSS THE SAVOY SILL
Feet
800
700
600
500
400
300
250
Greta
Basalt
Dolerite
Greta
Branxton Beds
Greta
F
G
0
40
80
Chains
Horizontal Scale
Feet
900
800
700
600
500
Greta
Series
Syenite
Dolerite
Pringles Ck
Dolerite
Basalt
Greta
D
E
0
20
40
Chains
Horizontal Scale
Feet
1000
500
Greta
Series
Basalt
Dolerite
Greta
Pringles Ck
Branxton Beds
Basal Sandstone
C
B
0
20
40
Chains
Horizontal Scale
Feet
1000
900
800
700
600
500
Saddlers Ck
Upper Coal
Mulbring Beds
Branxton Beds
Greta
Dolerite
a
b
c
Syenite
d
Bore 183 ft
Possibly Syenite here
Savoy T.S. 1047 ft
Syenite
Greta
Coal
Measures
Dolerite
Basalt
Pringle's Creek
Greta
Branxton Beds
Basal Sandstone
A
B
20
0
20
40
60
80
Chains
Horizontal Scale

Fig. 4.

part of the Muswellbrook Coalfield by a white coarse-grained basal sandstone of the overlying Branxton Stage of the Upper Marine Series.

The concordant nature of the upper contact is particularly well shown along Pringle's Creek, where the boundary between the dolerite and the overlying shale outcrops just as if it were the boundary between two conformable sedimentary formations. The dip is E.S.E. at eight degrees (see sections AB, BC, and DE). This condition continues across Pringle's Creek to the south of the Savoy hill, the dip changing from a southerly one in the creek to S.W. at eight degrees near the hill. The upper surface of the sill must, therefore, be curved gently convex upwards at this point (section FG).

A traverse of the lower contact at the northern end of the sill outcrop and of the western edge north of the trigonometrical station shows that the base of the dolerite also remains at the one stratigraphical level, conformable to the sediments (Plate II and section CB).

A shaft which has been sunk (either to prove a coal seam or to obtain a water supply) 20 chains north-east from the Savoy hill, gives confirmatory evidence of this. The shaft is situated adjacent to the western margin of the sill outcrop, is about 145 feet deep and appears to have passed entirely through coal measure strata.

The contact appears to be transgressive, however, for a limited distance north-west and west of Savoy trig. station. Passing westward from the shaft referred to above, the boundary of the igneous rocks transgresses the strike direction of the sediments, and dolerite is found below the level at which it would be expected if it occurred as a simple sill. It might be inferred that the

habit of the dolerite was phacoidal at this point, but in the same creek which was referred to as showing the sharp dolerite-syenite contact (whilst the exposures are not very good) one gets the impression that the dolerite transgresses the bedding planes of the westerly-dipping Greta Coal Measures.

The shape of the syenite outcrop, its sharp contact with the dolerite and the topography seem also to indicate that the concordant nature of the intrusion is departed from at this point. This can be explained best by reference to the section AB. Near "a" on this section the Greta Coal Measures dip at 20 degrees a little to the south of west. The distance from "a" to "b" is only six chains, whilst "bc" is a steep scarp, the vertical difference between "b" and "c" being 150 feet. No syenite occurs *in situ* near "a", and there is no sign of a bending over of the syenite parallel to the westerly dip of the Coal Measures. On the contrary, immediately on reaching "c" one looks down a gentle dip slope "cd" (*vide* Plate III, Fig. 1). There is, therefore, little likelihood that the space above "abc" was ever occupied by syenite and that its form when intruded was much as we see it now. It follows that the syenite transgressed the bedding planes of the sediments if they had not already been transgressed by the dolerite.

The limited length of outcrop in a north-south direction over which transgressive contacts can exist, and the elongation of the syenite outcrops in an east-west direction suggest that this rock may have a partly dyke-like form. On the other hand, the general inclination of both the larger syenite outcrops in the direction of dip of the sediments, shows that after passing through the

dolerite the syenite spread out and took on the sill form. It evidently did not spread very far because there is no sign of it at the upper contact of the dolerite in the sediments, even quite close to the principal syenite outcrops.

We thus have a fairly clear picture of the form of the syenite portion of the intrusion. So far as the dolerite is concerned, its form must have been very similar to that of the syenite, and we have valuable confirmatory evidence afforded by a bore (windmill on map) put down in the saddle southerly from the trig. station. The bore appears to have passed through about 180 feet of dolerite (with possibly a little syenite near the top) and to have passed into indurated shale at that depth.* This thickness of dolerite (considered in relation to the observed facts further south, where as already described its upper surface is covered convex upwards) is best explained by assuming that the dolerite spread out from the plug locally forming a phacoidal sheet (see section AB).

The outcrops in relation to contour are such that it is possible to say that the boundary of the sill from Savoy trigonometrical station to the north-east corner of the outcrop is close to the original limits of the intrusion, but elsewhere we have no knowledge of its actual limits which are hidden under a cover of sediments.

There are no exposures giving a direct section across the full thickness of the sill, but measurement shows that the thickness is between 275 and 300 feet (*vide* section CB). Unless the boundary of the plug of dolerite westerly from Savoy trigonometrical station is drawn too far west

* From information kindly supplied by Messrs. White Bros. of "Edinglassie".

on the section AB, the bore put down in the dolerite westerly from Savoy places a minimum of 200 feet upon the thickness of the sill at this point, where, also, the syenite has a thickness of about 100 feet.

Geological Age.

(In the following brief statement, unless specifically referred to, the term "basalt" does not include the basalts of the dykes and small sills.)

The petrological description shows that a close resemblance exists between the Savoy rocks and those from certain other alkaline intrusive masses which are held to be of Tertiary age.(6) The age of the dolerites and syenites is arrived at through their association with normal olivine basalts of which the age is directly ascertainable.

The basalts which cap the highlands around the Hunter Valley (and which cannot be distinguished from the olivine basalts of some of the plugs) are correlative with the basalts of the region referred to by Sussmilch as the Merriwa tableland.(7) Evidence of the geological age of these basalts is furnished by the fossil leaves, fruits and fishes which occur in beds beneath them. Summarized accounts of the Tertiary leads and the volcanic rocks associated with them are given by David(8) and by Andrews.(9) These authors show that a threefold development of Volcanic rocks may be recognised: (*a*) Newer basalts, (*b*) alkaline series, (*c*) older basalts ranging from Eocene to Pliocene in age. David (*loc. cit.*) also suggests that the alkaline series may be in part younger than the newer basalts. Woolcott considers the newer

gold bearing leads, such as those at Gulgong, to be from Upper Miocene to Lower Pliocene in age.[10]

It is certain that alkaline dolerite rocks intrude the olivine basalts of the tablelands in which the Hunter is incised, as the following observations show.

In 1911 W. N. Benson stated that theralitic types overlie "normal Tertiary olivine basalt" near Mount Barrington.[11] This area has since been visited by W. R. Browne, who states (verbally) that nepheline-bearing analcite dolerite occurs as sills intrusive into the olivine basalts. W. G. Woolnough also observed "dykes of coarse-grained olivine dolerite" including essexite intruding the "Tertiary basalt cap" at Mount Warrawalong ([11], pp. 184-185).

In 1929 a volcanic neck was noted by one of us (H.G.R.) near Wingen containing breccias and basalt like those in the Sydney district. These appear to have been intruded by a pipe-like mass of a syenitic rock similar to the aplitic types of the Hunter Valley sills. In 1931 also a composite sill of coarse-grained dolerite and "normal olivine basalt" was noted at Murulla. At this locality small dykes of the basalt appear to intrude the dolerite and the dolerite passes into a fine-grained contact facies very like the basalt. Further, it is impossible to distinguish the sill basalts from the basalt in the talus which is derived from the tableland flows.

Whilst there is, therefore, some doubt about the details in the local order of intrusion and extrusion of the igneous rocks, it is clear that all of them are of late Tertiary age, a most important conclusion in its relation to the tectonics of the region.

The argument thus briefly presented is a general one and must be supported by further petrological work, but as the detailed petrology of all the sills has not yet been completed, a full discussion of their geological age must be reserved.

We have not come to a final conclusion with regard to the geological age of the basalts of the small sills and dykes, and as these have yet to be fully described only a few brief comments are offered at this stage. These basalts are undoubtedly of the same age as those noted by one of us (H.G.R.) at Jerry's Plains, which W. R. Browne considers may be correlated with basalts in the Greta Coal Measures near Raymond Terrace.[12] He regards the Jerry's Plains basalts as interbedded in the Upper Coal Measures. We are not prepared to confirm or deny the correctness of this correlation. It is doubtful, however, if sufficient field work has yet been done to determine whether the basalts referred to by Browne are flows or sills. The age of these rocks relative to the sediments in which they occur is made difficult by the fact that the absence of contact phenomena does not necessarily imply that the basalts are interbedded, as the absence of alteration at the contact of Tertiary intrusives with Kamilaroi sediments is quite remarkable in some places. (Tests carried out in the laboratory of the Department of Mines, 1928, on shale from beneath the Carrington sill showed little alteration until temperatures approaching 1,000° C. were reached.)

W. R. Browne came to his conclusion mainly on petrological evidence, but it is considered by one of us (H.F.W.) that on the same basis many of the dyke basalts have a very close resemblance to some of the rocks included in the Garrawilla Series by E. J. Kenny (in lit.).

Kenny regards these as being largely contemporaneous lavas in the Jurassic,[13] though he has also stated that some of the rocks are probably intrusive.[14]

It may be possible to determine the age of these basalts from a consideration of tectonics, but we do not appear to be in a position at present to say definitely to which of the two earth movements which have affected the region they should be assigned. As stated on page 213, however, this evidence suggests a Tertiary or at least a post-Triassic age for the dyke basalts.

All that can be said at this stage is that the basalts are of late Kamilaroi age or younger, and that they may prove to be Jurassic or Tertiary.

Tectonics in Relation to Injection of Igneous Rocks.

The petrological research shows that there is no line of distinction between the syenite of the principal outcrops and that of the dykes. From this and the fact that the syenite occurs in sharply bounded dykes in the dolerite, it is clear that (i) the consolidation of the latter was complete before the injection of the syenite, (ii) differentiation of the magma had been effected in a reservoir removed from the place of intrusion prior to injection, (iii) the syenite was injected during a time of crustal stress, which was therefore of late-Tertiary age. The first and second of these points are discussed later (page 229).

With reference to the third, we are far from being in a position to make a satisfactory analysis of the stress directions of the region. It has been subjected to two well-marked orogenic movements, one of which is late Palæozoic and the other post-Triassic. The evidence for the former has been tranversed in some detail by

Osborne[15] and for the latter in brief by one of us (H.G.R.).[16]

Osborne (*loc. cit.*) gives the following trend lines as those which have been developed by the late-Palæozoic disatrophism in the Hunter region: (1) N. 15° W.-N. 20° W., (2) N. 30° W.-N.W., (3) almost due north and south, and (4) N. 20° E.

It would appear, however, from evidence already given[16] and from that briefly reviewed below, that there must still be considerable doubt as to the relative importance of late-Palæozoic and post-Triassic earth movements in producing structures with these trends. For instance, the Lochinvar dome, undoubtedly in part a late-Palæozoic structure, has a fault (Matthew's Gap) developed on its western side parallel to its principal axis, which involves the Triassic equally with the Permian.[16] The Wingen fault also has a strike a little to the north of west, and is almost certainly post-Triassic.

These are major structures. A study of the secondary structures leads also to significant conclusions, but it is only possible to deal very briefly with these in the present paper. The main secondary structures are:

A. Joints and syenite dykes in the Savoy sill. Strike directions: (i) N. 35° W., (ii) E. 5° N.

B. Basalt dykes (Text-fig. 1). Strike directions: (i) N. 15° E. to N. 35° E. (dominant), (ii) meridional, (iii) N. 20° W., (iv) E. 6° N. to E. 20° N. (common).

C. Thrust faults: (i) At Grasstree striking N. 25° W. to N. 30° W. (described in detail by H.G.R.[17]); (ii) at Antiene. Average of strikes about E. 15° N. (see Text-fig. 1).

The basalt dykes striking N. 15° E. appear to cut across the thrust faults at Antiene.

It has been shown above that the structures of Group A are of late Tertiary age, and the thrust faults may be correlated tentatively at least with the Hunter thrust of post-Triassic age.[17] It will be noted that there is fair agreement between the strike directions of these two groups of structures, notwithstanding that one is due to tension and the other to compression. Some of the basalt dykes fit in with the trends of Groups A and C also, and although the dykes with the dominant direction N. 15° E. do not, there is evidence at Antiene that the dykes with this strike appear to cut across some of the faults. Moreover, it is reasonably certain that all the dykes are of the one age. There is, therefore, no reason yet apparent why all the secondary structures may not be regarded as owing their origin to diastrophic disturbances of post-Triassic (probably largely Tertiary) age.

Now, if the trends of A, B and C be compared with those quoted from Osborne as characterising the late-Palæozoic diastrophism, it will be seen that there is a rather remarkable agreement between nearly all of them. If this means that earth movements have been similarly directed in both late-Palæozoic and post-Triassic time, it is difficult to see how, in the absence of other evidence, we can say which of the two played the more important part, the mere citation of a trend being of no value.

So far as the Muswellbrook dome is concerned, it may have originated in the late Palæozoic and become markedly accentuated in the late Tertiary. The dolerite was apparently injected during the first stages of the later movement. The intrusion was plug-

like in the first instance, but spread out, conforming to the bedding planes of the incompetent shales of the Greta Coal Measures. The existence of a competent sandstone bed in the Branxton stage of the Upper Marine was probably an important factor in determining the horizon of the intrusion (*vide* [18]). This it may have done directly or indirectly depending upon the age of the basalt overlying the dolerite. Thus if the basalt is older than the dolerite, the sandstone may have caused the former to take on the sill form in the first place, the basalt in its turn determining the horizon of the dolerite.

After the dolerite had consolidated, jointing developed under the influence of regional stresses in directions N. 35° W. and E. 5° N., *i.e.,* inclined to each other at 120 degrees. At the same time the syenite was injected, for the fact that the joints extend across the dykes in places shows that the intrusion of the syenite must have taken place during the period of joint formation (*vide* [19]).

It is possible that the extension of the plan of the outcrop westerly from Savoy hill is also controlled by joints owing their origin to the same stresses.

Depth of Cover at the Time of Intrusion.

According to Sussmilch ([7], p. 42), "the basaltic eruptions appear to have immediately preceded the uplift of the tablelands (Kosciusko uplift) . . ." Thus the flows were poured out upon a peneplain which was subsequently uplifted to form a plateau or tableland, the dolerites being intruded at about the same time. In the Muswellbrook district this tableland is about 2,000 feet above present sea-level. (Woodlands T.S., 2,213 feet on the south side of the Hunter, is on Tertiary basalt;

Bell's Mountain T.S., 2,240 feet to the north-east of Muswellbrook, is on Kuttung rocks.)

Since all the major faults in the area under discussion are pre-Kosciusko (see Osborne, *op. cit.*, p. 451), and there is still basalt on the plateau, the difference between the height of Savoy T.S. (1,047 feet) and the present plateau level is a measure of the maximum amount of cover which could have been present when the intrusion took place. This depth of cover, about 1,150 feet, could only have been reduced by the depth of a pre-uplift valley which might have existed above the present Savoy hill. Of the existence of such a valley there is no evidence; on the contrary, the Savoy, Arthur and Ogilvie trigonometrical stations appear to lie on a ridge which was a pre-uplift divide.

It may be of interest to express the depth of cover in terms of the weight of the rock column. Of the 1,150 feet, a maximum of 650 feet would have consisted of Triassic sandstone and conglomerate (difference between heights of Arthur and Woodlands T.S.), and the remainder largely of shale (Upper Marine and Upper Coal Series). Taking the weight of a cubic foot of sandstone as 137 lb. and of a cubic foot of shale as 162 lb.,[20] the pressure per square foot at the horizon of the intrusion would have been approximately 75 tons.

PETROLOGY.

Three rock types are recognised: analcite dolerite, soda syenite and basalt.

Analcite Dolerite.

This rock forms the main mass of the sill, and although many specimens were collected and examined carefully,

no evidence could be found of gravitative differentiation in the portion exposed by denudation. It is somewhat soft, and unaltered specimens are difficult to obtain, even the freshest material from outcrops in watercourses, where the decomposed mantle has been removed by stream erosion, showing a considerable degree of alteration. There are strong reasons for the belief that the softening of the rock is not due to weathering alone, but to the effects of late magmatic processes. This point will be dealt with later in describing the individual minerals of the rock. In hand specimens the rock is seen to be holocrystalline, medium to coarse grained, and of a dark greenish-grey colour. Under the microscope it is seen to be composed mainly of plagioclase, titaniferous augite, ilmenite with interstitial alkali felspar, chlorite, analcite, kaolin, serpentine, talc, brown hornblende, biotite and quartz, and numerous small inclusions of apatite. The fabric is granular to subophitic.

Description of Minerals.

Plagioclase occurs as idiomorphic lath-shaped crystals 1 to 3 mm. in length, and is usually much altered, many crystals having been entirely replaced by kaolin and sericitic material. Twinning is much obscured by heavy deposition of kaolin, but both albite and Carlsbad types are shown. Symmetrical extinction angles of about 32° indicate that it is labradorite, having approximately the composition $Ab_{45}An_{55}$. Zoning is exhibited by some crystals and is of the normal type, the centres being of calcic and the margins of more acid kinds of felspar. A much altered alkali felspar occurs filling many of the interstices of the rock. Much of this material is un-

twinned and has a refractive index less than that of Canada balsam. As the norm indicates the presence of 7·23% of orthoclase, it is probable that the interstitial felspar contains both orthoclase and albite. The alteration of the alkali felspar is more pronounced than in the case of the labradorite, many areas being quite opaque through deposition of kaolin. One peculiar feature of the interstitial felspar is the occurrence of a few small patches of quite clear unaltered mineral obviously of late crystallisation, suggesting that the kaolinisation of the first formed felspars took place before the deposition of the last interstitial felspars. Distinct evidences of albitisation of labradorite are seen; in places the kaolinised labradorite crystals have a narrow margin of clear unaltered alkali felspar. This process, however, does not appear to have taken place extensively, for only occasional crystals are thus affected.

Augite.—A slightly purple coloured, faintly pleochroic variety occurring in sub-idiomorphic crystals and irregular grains, many of which are ophitically moulded on the felspar laths. The average grain size is 1 to 2 mm. in diameter. The amount present is considerably in excess of the 12% shown in the norm, most specimens examined containing in the vicinity of 25%. A most remarkable feature of the augite is that notwithstanding the high degree of alteration of the rock, it is as a rule quite fresh, and has suffered little or not at all. It occasionally shows a slight reaction rim where it is in contact with the alkaline interstitial materials. These rims are very narrow and indefinite and are apparently of a chloritic character.

Ilmenite is an important constituent, occupying about 5% of the volume of the rock. It occurs in its typical skeletal crystals mainly in the interstitial material, seldom included in the augite or labradorite. The late crystallisation of ilmenite and magnetite has been referred to by Teall[21] in describing the basalts of Franz Josef Land, and by Washington[22] in dealing with the Deccan Trap Rocks of India. Much of the ilmenite is intergrown with biotite and many crystals are coated with leucoxene. Similar ilmenite-biotite intergrowths in dolerite have been described by Tyrrell ([3], p. 553), who states that they are to be explained by a reaction between the ilmenite and the residual sodic liquor.

Interstitial Material.

The interstitial material which occupies probably 25% of the rock space contains, besides the alkali felspars already alluded to, chlorite, kaolin, biotite, brown hornblende, analcite, quartz, serpentine, talc and carbonates, and numerous tiny prismatic crystals of apatite.

Chlorite is the most abundant interstitial mineral, and can be seen partially replacing brown hornblende and biotitie, and also forms pseudomorphs after biotite in which traces of the cleavage planes of the original biotite are still visible. Most of it, however, occurs as indefinite scaly or fibrous masses, filling some of the interstitial spaces of the rock.

Kaolin is seen to be derived from both the felspars and analcite, and some crystals of these minerals are so heavily charged with it as to be opaque. Kaolinisation of the felspars has been somewhat selective, most of the zoned labradorite crystals having been most affected

along their more acid margins. As before mentioned, there is distinct evidence that the process of kaolinisation should be regarded as of late magmatic origin, as the last formed felspars are quite unclouded.

Biotite is not plentiful in the rock. It occurs as small flakes often associated with the ilmenite. It is strongly pleochroic and its cleavage planes often show distortion. Much of it is altered to chlorite, the change being preceded by a change to a green coloured biotite, which then changes to typical chlorite.

Brown hornblende is rare, most of it having been altered to chlorite. It is pleochroic in shades of brown, brownish-yellow, and green, and always partly chloritised. Some of the chlorite shows two sets of cleavage traces intersecting at about 60°, indicating that it represents altered hornblende.

Analcite occurs very sparingly, filling some of the triangular interstices of the rock. It is nearly all clouded by decomposition, and some of it shows weak anomalous double refraction.

Quartz.—A very small amount of quartz is present in the rock. It occurs both as irregular interstitial masses and as thin shells around felspar crystals. The second method of occurrence is interesting, and lends weight to Fenner's[23] hypothesis that quartz and micropegmatite in basic rocks are the results of interaction between late magmatic mineralisers and earlier formed minerals. In the present instance it is thought that the kaolinisation of the felspar may have supplied the silica to form the quartz. It will be noticed that quartz is absent from the norm.

Serpentine is present in small amounts. It is of a pale yellowish-green colour, and some is recognisably pseudomorphous after olivine.

Talc occurs in tiny scales replacing some of the serpentine.

Carbonates are rare, and occur mainly in tiny veinlets associated with sericitic material in the felspars.

Apatite forms small acicular to prismatic crystals up to about 1·5 mm. in length, and is more abundant in the interstitial material than in the labradorite and augite.

Order of Consolidation.

The order of consolidation appears to be somewhat as follows:

> Labradorite, augite, olivine, ilmenite, biotite, hornblende, apatite, alkali felspars, analcite, quartz.

The hornblende probably crystallised about the same time as the biotite.

There was much overlap between the crystallisation of the interstitial minerals, and it is difficult to make out the exact order in which they consolidated. The apatite commenced to crystallise early and continued till most of the interstitial material was formed. The reversal of the normal order of consolidation in dolerites is fairly common. In N.S.W. similar orders of consolidation have been noted in the Prospects Mass,[(24)] the theralitic dolerite from Bombala ([(6)], pp. 377-378), and the large dolerite sills of the Coonabarabran Area (H.F.W., in lit.).

The development of chlorite, serpentine, talc, and kaolin should be regarded as a late magmatic process, and possibly the analcite, alkali felspar and quartz may,

in part, have been derived by interaction between the active mother liquor and the solid crystalline phase of the cooling rock. The late crystallisation of apatite and its consequent frequent inclusion in the interstitial material implies the presence of much fluorine or chlorine in the residual liquors. The action of a hot solution rich in fluorine doubtless caused changes in the earlier formed silicates and would be quite capable of leaching them of part of their silica content which could later have consolidated as quartz. Browne[(24)] implies some such origin for the alkali felspars in the Prospect dolerite. Fenner ([(23)], p. 753), in his paper on the volcanic rocks of the Katmai region of Alaska, summarises much of the literature dealing with the subject of the influence of magmatic gases on the crystallisation of igneous rocks and holds them responsible for the development of quartz and micropegmatites in the interstitial spaces of dolerites.

The late crystallisation of ferromagnesian minerals in basic effusive rocks is explained by Daly[(25)] as being due to the presence of gas fluxes in the vents, thereby lowering the freezing point of the lavas and thus lengthening the temperature interval during which femic minerals may form. Some such process has probably favoured the late solidification of the augite, hornblende and biotite in the dolerite from Savoy.

Soda Syenite.

The relationship of the syenite to the dolerite has been described; the junction between the two is probably quite sharp as the main mass of syenite does not exhibit increasing basicity with increasing depth, and the dolerite is

not noticeably more acid near the contact than in the lower portions, and small sharply bounded veins of syenite have been seen occupying joint fissures in the dolerite (see p. 202 and Fig. 3).

The syenite is a medium to fine grained, cream coloured holocrystalline rock, somewhat miarolitic in the upper portions of the main mass, but quite dense lower down. The drusy cavities are filled with quartz crystals, chalcedony or calcite. Under the microscope it is seen to be composed of alkali felspar which make up about 75% of the rock, with interstitial quartz, micropegmatite, indefinite patches of hematite, and a very small amount of each of soda amphibole, biotite, apatite, and ilmenite. The rock is even grained and has a granitic texture.

Description of Minerals.

Felspars are nearly all untwinned, but a few crystals show fine albite twinning and many exhibit either a fine cross-hatching or a "moire" extinction. The index of refraction is below that of Canada balsam and extinction angles are all low (about 5°). From the high Na_2O percentage and the high albite content of the norm, it is certain that much of the untwinned felspar must be soda orthoclase, as very little definite albite is present. Most of the felspar crystals are clouded through deposition of kaolin, and in some specimens examined the deposition of kaolin has been so heavy as to render the rock opaque. Some of the kaolinised crystals are surrounded by rims of clear albite, which exhibit albite twinning and have a refractive index slightly higher than the orthoclase or anorthoclase, but lower than Canada balsam. Rims of quartz are also common, and where felspar is in contact

with quartz it is invariably more heavily charged with kaolin than elsewhere, suggesting that the quartz may have been formed by the kaolinisation of felspar.

Quartz.—This mineral occurs mainly in micrographic intergrowth with felspar, but also as irregular interstitial grains. It is most plentiful in the drusy portions of the rock.

Hematite occurs as reddish-brown opaque masses, in places clearly resulting from the alteration of ferro-magnesian minerals, whilst in others a core of magnetite or ilmenite can be seen.

Soda amphibole occurs most plentifully in specimens containing least quartz. It is apparently of early crystallisation, and builds subidiomorphic crystals up to 0·5 mm. in length. It is strongly pleochroic, the colours observed being pale brownish-green, dark brownish-green, and bluish-grey. The extinction angle is about 12°, indicating that it is arfvedsonite.

Biotite is a very rare constituent, and is usually of a very pale yellowish-brown colour.

Apatite occurs as tiny rod-like crystals plentifully scattered throughout the rock. As in the case of the dolerite, it appears to have crystallised rather later than most of the felspar.

Ilmenite occurs mainly as skeletal crystals enclosed in hematite.

Calcite occurs chiefly filling small dusy cavities and veins, but also filling some of the triangular spaces between the felspar crystals.

Chalcedony in its typical cryptocrystalline form occurs sparingly in a similar manner to the calcite.

Order of Consolidation.

Owing to the high degree of alteration and small amounts of ferro-magnesian minerals, their consolidation relationship is not clear. It is evident that the orthoclase and soda orthoclase enjoyed considerable freedom in crystallisation and that quartz and albite crystallised late, the quartz mainly in the interstices, but partly in micropegmatite, and the albite surrounding and possibly replacing orthoclase and soda orthoclase.

Harker[26] dealing with the Tertiary igneous rocks of Skye, states that "the association of druses, generally of small size, with xenoliths is a very general phenomenon." No xenoliths, however, are to be seen in the Savoy syenite, and the association of quartz and miarolitic structure are much more likely to be the results of magmatic gas action as is described by Fenner ([23], p. 759) in the case of the Virginian dolerites of Triassic Age. At Savoy the miarolitic structure is almost exclusively developed near the top of the sill where concentration of gases might be expected to have taken place.

Basalt.

The exact relationship of the basalt to the dolerite and syenite cannot be determined from field evidence. It is uncertain whether it represents a chilled margin of the dolerite or an earlier intrusion.

In hand specimens the rock is seen to be soft and weathered; it is buff to brown in colour, fine grained and in some places appears to be slightly amygdaloidal. Under the microscope it is seen to be composed mainly of basic plagioclase laths averaging about 25 mm. in length, with much indefinite interstitial material heavily charged with

hematite. Ferro-magnesian minerals are represented only by the chloritic material and hematite in the groundmass. Close examination of the interstitial material shows the presence of a little comparatively fresh alkali felspar, some chalcedony and calcite. Many minute crystals of apatite are also present. The amygdaloidal areas are seen to be more in the nature of irregular drusy cavities than smooth steam holes. The filling is usually either chalcedony or calcite, and each cavity is surrounded by a zone of hematite.

The type of alteration of the basalt is similar to that found in the syenite which shows alteration of ferro-magnesian minerals to hematite instead of to chlorite as in the case of the dolerite.

Chemical Composition.

The dolerite and syenite were submitted to analysis, but it was thought that no useful purpose could be served by analysis of the basalt, owing to its high degree of weathering. Analyses of similar dolerites and syenites are quoted for comparison.

It will be noted that the silica percentage of the dolerite is rather higher than is usual in similar rocks, but, apart from this feature, the analysis agrees fairly well with that of the Prospect paleo-essexite, which has been regarded as the undifferentiated type rock. The potash percentage is very close to that of the Prospect rock and, coupled with the presence of alkali felspars, shows the rock to have Essexitic affinities. Owing to the higher silica percentage, felspathoids are almost absent from the Savoy rock. The norm calculated from the analysis agrees fairly closely with the minerals pre-

ANALYSES.

	I.	II.	III.	IV.	V.	VI.
SiO_2	60·76	49·50	46·26	45·57	44·69	56·44
Al_2O_3	14·23	16·46	13·36	14·95	14·17	15·54
Fe_2O_3	5·40	3·70	2·34	2·82	3·35	3·27
FeO	0·99	6·12	10·53	7·35	10·86	3·67
MgO	0·80	5·75	8·87	6·19	6·41	1·73
CaO	4·36	8·14	9·18	8·27	10·28	4·16
Na_2O	5·30	4·40	3·27	4·33	3·64	5·81
K_2O	3·67	1·15	1·23	2·16	2·01	4·27
H_2O+	1·47	2·69	2·08	3·93	2·53	2·06
H_2O-	0·35	0·87	0·15	0·97	1·01	0·44
TiO_2	0·90	0·76	1·78	2·41	0·46	1·16
P_2O_5	0·26	0·48	0·42	0·67	0·45	0·83
CO_2	1·60	0·16	0·06	0·18	Nil.	0·97
MnO	0·18	0·16	0·12	0·31	0·31	—
Cl	Trace.	Trace.	—	—	—	—

NORMS.

	I.	II.	III.	IV.	V.	VI.
Quartz	9·12					
Orthoclase ..	21·68	7·23	7·23	12·79	11·7	25·6
Albite	44·54	26·72	20·44	21·48	8·6	49·2
Anorthite ..	4·17	21·68	18·07	15·01	16·4	3·4
Nepheline ..	—	5·68	3·98	8·24	12·1	—
Diopside ..	8·50	12·14	20·15	17·27	26·5	4·5
Hypersthene ..	—	—	—	—	—	4·1
Olivine	—	11·09	19·50	10·33	14·6	—
Magnetite ..	0·70	5·34	3·48	4·18	4·9	4·9
Ilmenite	1·67	1·52	3·34	4·56	0·9	2·3
Hematite ..	4·96	—	—	—	—	2·2
Apatite	0·67	1·34	1·01	1·68	1·0	2·2

I. Soda syenite—Savoy Hill, Muswellbrook. W. A. Greig, Analyst.

II. Dolerite—Savoy Hill, Muswellbrook. W. A. Greig, Analyst.

III. Paleo-Essexite—Prospect, N.S.W. Jenson, Jevons, Taylor and Sussmilch, *Proc. Roy. Soc. N.S.W.*, 1911, Vol. XLV.

IV. Scottish Tescherite—average of 5 samples. Tyrrell, G. W., *Geol. Mag.*, 1923, p. 245.

V. Crinanite—Howford Bridge, Mauchline, Scotland. Tyrrell, G. W., *Q.J.G.S.*, Part 3, 1928, Vol. LXXXIV, pp. 557-9.

VI. Analcite Syenite—Howford Bridge, Mauchline, Scotland. Tyrrell, G.W., *Q.J.G.S.*, Part 3, 1928.

sent in the rock, the main differences being that analcite is present in place of nepheline, whilst augite, biotite, serpentine, hornblende and chlorite take the place of diopside and olivine.

The analysis of the Savoy soda syenite agrees fairly closely with that of the Howford Bridge analcite syenite, but shows a slightly higher silica content. But for the presence of quartz in the Savoy rock, the norms also are in fairly close agreement. The norm is very similar to the mode, the only difference being that the diopside of the norm is represented in the rock by soda amphibole and a little mica. It is quite possible that some of the hematite present in the rock represents completely oxidised pyroxene, in which case there would be even less difference between the normative and the actual mineral composition of the rock.

Relationship of the Syenite to the Dolerite.

So many instances of the occurrence of syenitic veins in dolerite are known that it must be regarded as quite a normal phenomenon. The best known example in N.S.W. is the Prospect intrusion described by Jevons[(2)] and his co-authors; Tyrrell[(3)] has described veins of analcite syenite in doleritic rocks in Ayrshire. Syenite veins in trachydolerite have been noted by Ichimura[(4)] in Korea and Northern Manchuria, and they are also known to occur in the large sills and laccolites of California.

Many writers, most notably Bowen[(27)] and Tyrrell ([(3)], p. 565), seek to explain this phenomenon on the crystallisation and filter pressing hypothesis whereby the more basic constituents of the magma crystallised, first

forming a "sponge" of basic crystals filled with an acid mother liquor. The sponge has been assumed to contract on cooling, and the mother liquor to be driven out by earth movements, pressure of superincumbent rocks or contraction, to solidify in cooling cracks or regions of earth tension. This hypothesis has been strongly opposed by Fenner ([23], p. 759) who points to the fact that in many dolerites and basalts the basic minerals crystallise late. He doubts whether the mere crystallisation of a basaltic magma would at any time yield an acid residuum approximating a syenite in composition, and explains the aplitic veins as due to the magmatic waters containing mineralising agents, removing certain constituents from the earlier formed rocks and depositing them later in cracks and joints. He further supposes the magmatic waters and mineralisers to be the cause of the alteration of the syenitic rocks and the cause of drusy cavities and development of secondary minerals in them.

Daly ([25], p. 396) has drawn attention to the frequent association of trachytic lavas with basaltic types, as well as syenitic veins in dolerites, and seeks to explain all the rocks of the syenite clan as due to contamination of a basaltic magma by assimilation of sediments at great depths, followed by differentiation and the subsequent intrusion or extrusion of first the basic and then the acid phase so formed.

At Savoy there is no evidence of differentiation *in situ*, and the sharp junctions of some of the smaller veins of syenite in the dolerite indicate that the syenite was injected after the dolerite had completely solidified. A microscopic examination of the junction of one of the

veins and the dolerite shows no signs of intermixing of the felspars, such as might be expected were the syenites formed from an alkali-rich mother liquor extruded from the spaces of the dolerite. Had the syenite originated by means of "filter pressing" of the dolerite, a trachytoid arrangement of the minerals of the "sponge" ought to be evident due to the contraction following the extrusion of the mother liquor; no such texture can be observed, however, in any specimens of the dolerite so far collected. The weight of evidence seems to point to the fact that the syenite differentiated from the dolerite in a deep seated magma chamber and was injected at some considerable time interval after the dolerite had solidified. The injection of the syenite was accompanied by magmatic waters and gases that were responsible for the kaolinisation of the felspars of the syenite, the development of druses in its upper portion, the leaching of its ferromagnesian minerals, and probably also part of the alteration of the dolerite as well. The arrangement of the small dykes of syenite in the dolerite suggests that they occupy a system of joints of tectonic origin, rather than shrinkage cracks (see p. 211).

In considering the relationship of the syenite and dolerite it is interesting to note that in the case of the Tertiary eruptive rocks of eastern Australia, alkaline trachytic rocks are frequently associated with basalts and usually appear to post date the latter by some considerable time. As there is evidence that the Savoy intrusion is of Tertiary Age, it seems probable that the dolerite should be regarded as the hypabyssal equivalent of the older basalts and the syenite as representing the later trachytes. This matter, however, will be dealt with

more fully in a later paper dealing with the whole of the intrusive rocks of the Muswellbrook-Singleton area in which the problem of their ages will be more fully discussed.

Summary.

The Savoy intrusion, one of a number of doleritic igneous masses in the Muswellbrook-Singleton coalfield, is described in detail. It is shown to be mainly a concordant intrusion into the Greta Coal Measures, partly of the simple sill type and partly phacoidal, of which the feeding channel is to some extent exposed. The main mass of the sill consists of dolerite with syenite veins intruding it. These veins are of two types: one stratiform, approximately parallel to the roof of the sill, and the other occupying joints in the dolerite. Syenite also forms the upper portion of the sill adjacent to the feeding channel.

Evidence for the Tertiary age of the intrusion is given. The mode of occurrence of the syenite and the secondary structures of the Muswellbrook district are discussed in relation to the tectonic geology of the region.

In the petrological section of the work, three types of rock are recognised, analcite dolerite, soda syenite and basalt. These are described in detail. Rock analyses of the dolerite and syenite are given and comparisons made with rocks of similar types from Prospect, New South Wales, and from Scotland.

The absence of evidence of differentiation *in situ* at Savoy is emphasised in discussing the relationship between the syenite and the dolerite. It is also pointed out that the injection of the former was accompanied by magmatic waters and gases that were responsible for the

kaolinisation of the felspars of the syenite, the development of druses in the upper portion, the leaching of its ferro-magnesian minerals and probably also part of the alteration of the dolerite as well.

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[12] Browne, W. R.: "An Outline of the History of Igneous Action in N.S.W. till the Close of the Palæozoic Era", *Proc. Linn. Soc. N.S.W.*, Vol. LIV, Part I, p. xxix, 1929.
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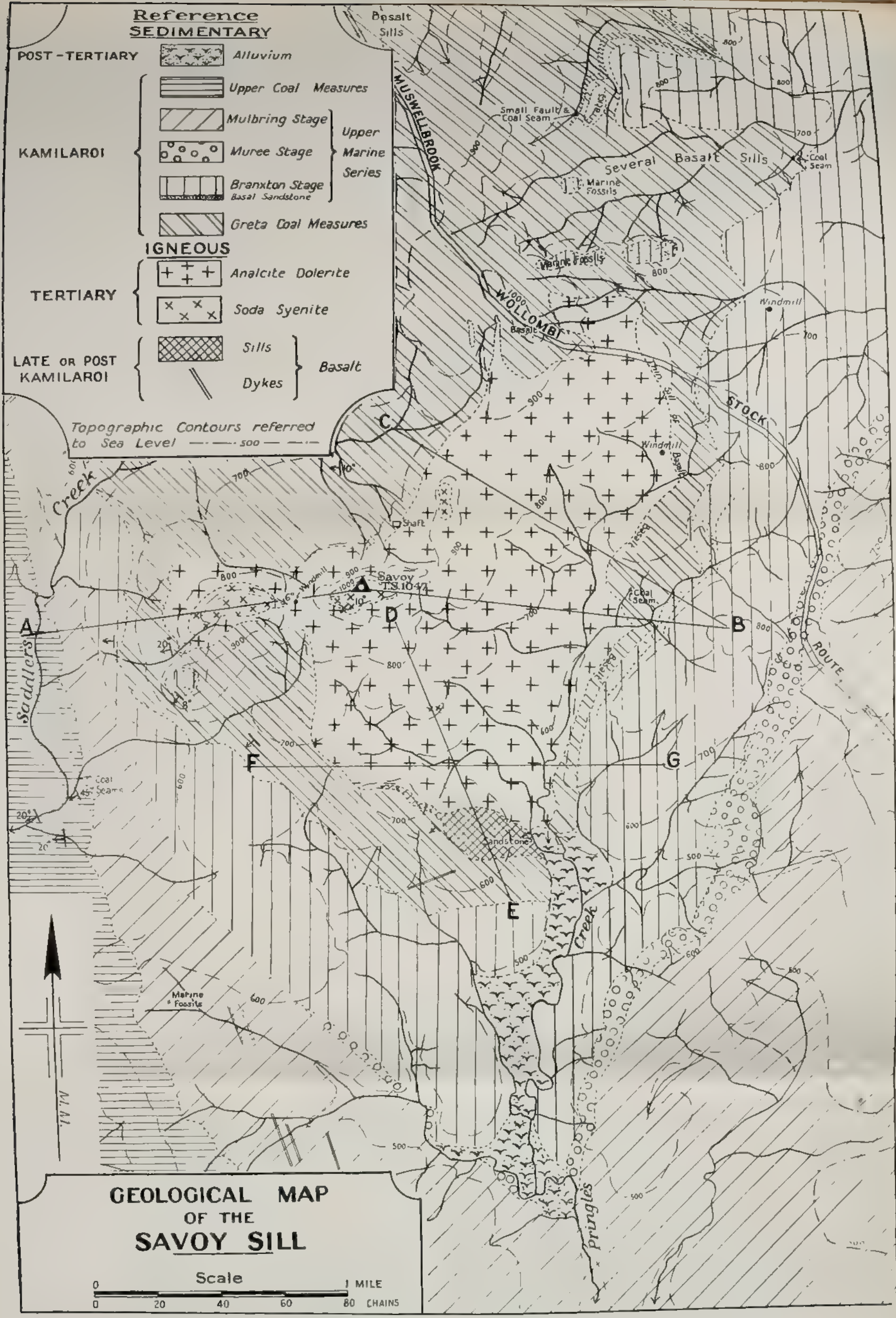
Reference
SEDIMENTARY
POST-TERTIARY
Alluvium
Upper Coal Measures
Mulbring Stage
KAMILAROI
Muree Stage
Upper Marine Series
Branxton Stage
Basal Sandstone
Greta Coal Measures
IGNEOUS
TERTIARY
Analcite Dolerite
Soda Syenite
LATE OR POST KAMILAROI
Sills
Dykes
Basalt
Topographic Contours referred to Sea Level 500
MUSWELLBROOK
WOLLOMBI
STOCK
ROUTE
Several Basalt Sills
Small Fault & Coal Seam
Marine Fossils
Savoy T.S.1047
Saddlers Creek
Pringles Creek
Sandstone
Coal Seams
Windmill
Shaft
GEOLOGICAL MAP OF THE SAVOY SILL
Scale
0
1 MILE
0 20 40 60 80 CHAINS
M.M.

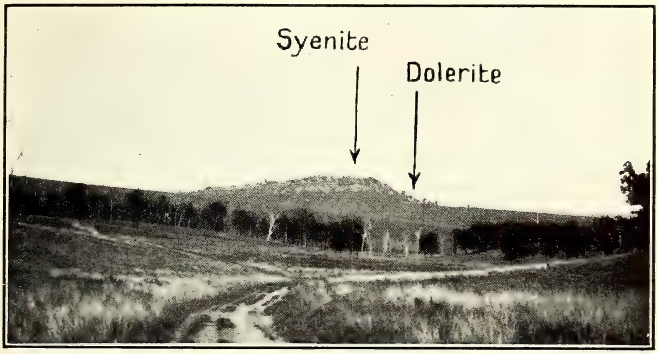

Fig. 1.

Photo.—H. G. Raggatt.

Fig. 2.

Photo.—F. W. Booker.

Fig. 1.

Fig. 2.

Fig. 3.

[26] Harker, A.: "Tertiary Igneous Rocks of Skye", *Mem. Geol. Surv. Gt. Brit.*, p. 185, 1904.
[27] Bowen, N. L.: "The Later Stages of Evolution of Igneous Rocks", *Supp. Jour. Geol.*, Vol. XXIII, p. 90, 1915.

Explanation of Plates.

Plate II.

Detailed Geological Map of the Savoy Sill. (Mr. M. Morrison, assisted by Messrs. F. W. Booker and C. St. J. Mulholland, made a preliminary survey of the sill area in 1925, but the detailed work on which the present map is largely based was not carried out until 1929. This was done by one of us (H.G.R.), assisted by Mr. F. W. Booker.)

Plate III.

Fig. 1.—View, looking south, of the syenite hill west of the Savoy Trigonometrical Station, showing the scarp on the western side and the general dip surface to the east. (Compare with Section AB of Text-fig. 4.)

Fig. 2.—Aplitic veins (picked out in white) in dolerite as exposed on the right bank of Pringle's Creek. One vein is dyke-like, but the majority are arranged approximately parallel to the roof of the sill.

Plate IV.

Fig. 1.—Dolerite by ordinary light. Idiomorphic labradorite laths with augite sub-ophitically moulded on them. The grey areas are mainly kaolin and the black portion of the photograph represents chlorite and ilmenite. Several triangular areas of alkali felspar occupying spaces between labradorite crystals are included in the photograph. × 16.

Fig. 2.—Dolerite viewed between crossed nichols. The darkness of the interstitial material is largely due to the heavy deposition of kaolin in the alkali felspars. × 16.

Fig. 3.—Soda syenite between crossed nicols, showing micropegmatite areas surrounded by soda orthoclase. The "moiré" extinction of the soda orthoclase is well known. × 32.

THE CRYSTAL STRUCTURE OF INDIUM.

By Francis P. Dwyer, B.Sc.,
and David P. Mellor, M.Sc.

(Read before the Royal Society of New South Wales, July 6, 1932.)

Since the only two observations on the crystal structure of indium are contradictory, it is clear that the structure needs reinvestigation. Sachs,[1] on the basis of goniometric measurements made on small crystals of the electro-deposited metal assigned them to the cubic system. On account of the smallness of the crystals and the pitted nature of their surfaces, observations were difficult, and they were confined to the angle between what were considered to be the (111) faces. As the mean of six measurements, the angle between these faces was found to be 70° 48′, a value which agrees closely with that calculated for the angle between the octahedral faces of a cubic crystal. On the other hand, Hull[2] interpreted the lines of a powder photograph made on a sample of impure indium as arising from a face-centred tetragonal structure with an axial ratio of 1·06. The validity of this structure has recently been queried by Wyckoff.[3] In view of the fact that allotropic modifications of manganese[4] and

[1] *Zeit. f. Kryst.*, 38, 495 (1904).
[2] Hull: *Physical Review*, 17, 571 (1921).
[3] Wyckoff: "The Structure of Crystals", 2nd Ed. (1931), p. 209.
[4] Bradley: *Phil. Mag.*, 50, 1018 (1925). Westgren and Phragmén, *Z. Physik.*, 33, 777 (1925). Persson and öhmann, *Nature*, 124, 333 (1929). Sekito: *Zeit. f. Kryst.*, 72, 406 (1929).

chromium[5] have been produced by electrolysis, it appeared possible that the divergence of the above observations on the crystal form of indium might be due to the existence of two forms of the metal, one of which was an electrolytic modification. Therefore, powder studies have been made on specimens of indium which have been prepared both by electrolysis and cooling down from the molten state.

The Production and Measurement of Powder Photographs.

Copper $K_{\alpha 1 \alpha 2}$ radiation from a Shearer tube operated at 25,000 volts and 10 milliamperes was used. The K_β radiation was removed by means of a nickel filter which also served as a window to the tube. The camera, of radius 5·700 cm., was calibrated by means of powdered electrolytic copper. The lattice constant adopted for copper was 3·608 A.U.[6] Small errors due to the width of the specimen were also corrected for by the method due to Kolkmeijer.[7] The lines on all films were measured with a Hilger measuring machine.

Material.

Approximately 0·6 gm. of commercial indium was dissolved in dilute hydrochloric acid and evaporated to dryness on a water bath. The indium chloride was then carefully heated on a sand bath to 150° C. to remove

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[5] Ollard: *Metal Ind.* (London), 28, 153 (1926). Ollard and Bradley, *Nature*, 117, 122 (1926). Macnaughton: *Metal Ind.*, 28, 175 (1926). Sillers: *Trans. Amer. Electrochem. Soc.*, 52, 301 (1927). Sasaki and Sekito: *Trans. Amer. Electrochem. Soc.*, 59, 437 (1931).

[6] "*Gitterkonstanten* 1931"; Neuberger: *Zeit. f. Kryst.*, 80, 103 (1931).

[7] "*Prazionsbestimmung der Dimensionen von Krystallgittern*", 80, 63 (1931).

the last traces of water. The anhydrous salt was dissolved in about 25 c.c. of absolute alcohol and a slight excess of pyridine added. The compound $[InCl_3(C_5H_5N)_3]$, which immediately crystallised out, was filtered off, washed with alcohol and then hydrolysed with a solution of ammonium chloride. By this means the peptisation of the resulting indium hydroxide was avoided. The indium hydroxide was dissolved in dilute sulphuric acid and ammonia was added until a precipitate just formed. This solution gave no test for iron when treated with ammonium thiocyanate. One c.c. of formic acid was added and the solution was then electrolysed between platinum wire electrodes with a current of 0·8 amp.

In order to prevent the formation of an alloy with the platinum, indium was deposited only on the tip of the cathode. For the first 8 hours the cell voltage was kept below 4 volts in order to plate out impurities such as copper. The resulting soft spongy metal was melted *in vacuo* and cast into forms from which the powdered metal was prepared by filing. Specimens for the study of the electrolytic form of the metal were prepared by plating out the metal on very fine silver wires under different conditions of temperature and current density. Two specimens were prepared by electrolysis at a temperature of approximately 0° C. with current densities of 0·7 amp./cm.^{2} and 16·6 amps./cm.^{2} respectively. In order to reproduce as closely as possible the conditions of electrolysis maintained by Thiel,[8] whose material was the subject of Sachs' investigation, two deposits were pre-

[8] *Zeit f. Chem.*, 40, 280 (1904).

pared at 60° C. with current densities of 0·76 amp./cm.^{2} and 30·3 amps./cm.^{2} respectively.

Powder Photographs of Electrolytic Indium.

In none of the four photographs of the specimens just described was there any suggestion of a pattern which could be attributed to a cubic structure. In all cases the lines could be interpreted as arising from a face-centred tetragonal structure similar to that of γ manganese.

Powder Photographs of Indium Prepared by Cooling the Molten Metal.

These were identical with the photographs of the electrolytic material. The lines in all photographs were quite sharp. Since impurities may have affected the value of the lattice constants determined by Hull, it was decided to redetermine these constants for carefully purified materials and to evaluate the axial ratio more precisely than is possible by the graphical method. Two determinations in substantial agreement were made on cameras of different radii. Measurements with the large camera only are given. The results are summarised in the following table.

The values of $\sin^2\theta$ in Table 1 satisfy the relation:

$$\sin^2\theta = 0{\cdot}2814(h^2 + k^2) + 0{\cdot}02423(l^2) \quad \ldots\ldots\ldots \quad (1)$$

This relation and the absence of certain spectra show that the lattice of indium is face-centred tetragonal. The intensities, estimated only very approximately (visually), are in qualitative agreement with those calculated for the structure.[9] From the constants in

[9] Wyckoff: "The Structure of Crystals", 1st Ed., p. 201.

TABLE I.

Corrected θ.	Sin θ.	$\text{Sin}^2\,\theta$.	Spacing Observed.	Spacing Calculated.	Intensity Estimated Visually.	Intensity Calculated.	Index.
16° 29′	0·2836	0·0805	2·714 A.U.	2·713 A.U.	10·0	10·0	(111)
19° 36′*	0·3355	0·1125	2·295 ,,	2·294 ,,	2·0	0·3	(200)
27° 12′	0·4571	0·2089	1·684 ,,	1·682 ,,	3·0	0·6	(202)
28° 19′	0·4744	0·2250	1·622 ,,	1·622 ,,	0·5	0·1	(220)
31° 37′	0·5242	0·2747	1·470 ,,	1·470 ,,	1·5	1·2	(113)
33° 35′	0·5530	0·3060	1·392 ,,	1·393 ,,	5·0	2·1	(311)
34° 35′	0·5677	0·3222	1·356 ,,	1·357 ,,	1·0	0·4	(222)

*Lines corresponding to planes (002) and (151) were observed on different films but were too faint for measurement in this particular instance. Copper lines used for the calibration of the camera are also omitted.

equation (1) the following values for a_0 and c_0 may be calculated:

$$a_0 = 4{\cdot}588 \pm 0{\cdot}002 \text{ A.U.}$$
$$c_0 = 4{\cdot}946 \pm 0{\cdot}002 \text{ A.U.}$$

$a:c = 1{\cdot}078 \pm 0{\cdot}002$. Number of atoms per cell = 4.

Density (calculated from X-ray data) = 7·28.

Density (from standard determination) = 7·27.[10]

The coordinates of the atoms are as follows:

$$000;\tfrac{1}{2}\tfrac{1}{2}0;\tfrac{1}{2}0\tfrac{1}{2};0\tfrac{1}{2}\tfrac{1}{2};.$$

The distance between the atomic centres of the atoms situated at the centres and corners of the (001) faces is 3·28 A.U. The corresponding distance for the atoms situated at the centres of the (100) and (010) is 3·89 A.U. Apparently indium atoms in the metallic state do not possess spherical symmetry since the above face-centred tetragonal structure is the kind that would result from the close packing of prolate spheroids with axes in the ratio 1 : 1·078. In this lack of spherical symmetry, indium resembles zinc and cadmium. It would appear then that the atoms of zinc, cadmium and indium in the metallic state are not in the ionic condition since, in the case of cadmium oxide, for example, the nature of the inter-ionic forces[11] implies a spherical symmetry of cadmium and oxygen ions, unless any inherent lack of spherical symmetry is destroyed by thermal motions.

It is necessary to allow for this latter possibility, since there appears to be good evidence that the lower symmetry of nitrate and ammonium ions disappears through their rotation in the solid state.[12]

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[10] Richards and Wilson: Carnegie Institution Publications, No. 118, p. 13 (1909). *Zeit. f. Chem.*, 72, 129 (1910).
[11] *Trans. Far. Soc.*, 25, 406 (1929).
[12] *Nature*, 128, 410 (1931).

THE CHEMISTRY OF WESTERN AUSTRALIAN SANDALWOOD OIL.

PART II.

By A. R. PENFOLD, F.A.C.I., F.C.S.,

Curator and Economic Chemist, Technological Museum, Sydney.

(Read before the Royal Society in New South Wales, August 3, 1932.)

The publication of my Part I paper in the *Journal and Proceedings of the Royal Society of New South Wales,* Vol. LXII (1928), pages 60-71, provoked considerable controversy, but it is pleasing to note that the chemical composition of commercial Western Australian Sandalwood oil as revealed therein was subsequently confirmed by Dr. R. Coupechoux in his publication entitled "Contribution a l'etude de l'essence de Santal d'Australie," issued in 1931.

It is much to be deplored that a statement on page 62 of my publication (*l.c.*) reading "Curiously, however, the santalols were not detected in oils of our own distillation," recorded in good faith for purely scientific purposes, should have been made use or by commercial interests for trade purposes.

The principal object of this contribution is to record the results obtained in the examination of the interesting series of specimens of wood from various parts of the tree of *Eucarya spicata* (Sprague and Summerhayes) (Syn. *Fusanus spicatus,* R.Br. *Santalum spicatum,* A.DC.; *S. cygnorum,* Miq.), occurring in the different localities of Western Australia kindly furnished by Mr. S. L. Kessell, Conservator of Forests, Western Australia, in March, 1928 (see page 61, *l.c.*).

The various samples of wood were reduced as far as practicable to sawdust, but some of the roots and butts were difficult of reduction with the plant at our disposal.

The essential oils were obtained from each lot by steam distillation and not by means of solvent extraction. The yields recorded are relatively accurate, but it is pointed out that there is no evidence that the whole of the oil was removed from those specimens where the wood could not be reduced to the finest possible state of subdivision. An example is given in Sample "C" in Table "A," where the yields of both coarse and fine material are recorded, *viz.*, 1·6% and 2·4% respectively.

The chemical and physical characters of the various crude oils are set forth in Table "A."

The alcoholic bodies were prepared from each lot of oil enumerated in Table "A" by treatment of 100 grs. with equal weights of phthalic anhydride and benzene heated on a boiling water bath for two hours. The returns are furnished in Table "B," together with the distillation range and chemical and physical characters of each separate alcoholic constituent.

The other constituents of the oil were not further examined.

The alcohol, santalol, shown by Dr. R. Coupechoux to be the β form, was sought for in each specimen of alcohol by the following methods, *viz.*:

1. Oxidation to santalenic acid with potassium permanganate as per method given in *Jour. Proc. Roy. Soc. N.S.W.*, Vol. LXII (1928), page 68.
2. Preparation of the allophanate, as per procedure described on page 68 (*l.c.*).
3. Oxidation to santalal with Beckman's chromic acid mixture at room temperature.

Excellent results were obtained by methods (1) and (2), but some difficulty was experienced in the interpretation of the information obtained through the semicarbazones of the oxidation products in method (3), owing, no doubt, to the use of only 5 cc. alcohol—all that could be spared for the purpose. The yields and melting points of the derivatives obtained under headings (1) and (2) are recorded in Table "B."

Although the melting points of the various allophanates vary from 152° to 155-156°, mostly the latter, they represent the impure derivative of santalol. Repeated recrystallisation from ethyl alcohol resulted in the melting point being raised to 162-163° (*l.c.*, page 68).

The results obtained by oxidation with chromic acid are not included in this paper.

The results set forth in Table "B" show very conclusively that the alcohol santalol is present in considerable quantity in the oils obtained from the roots and butts. With the exception of sample "D," this alcohol was not detected in the oils obtained from the other lots of stickwood.

The specific gravity of the separated alcohols provides a very ready means of ascertaining the extent to which santalol is present. A perusal of the various specific gravities set out in Table "B" affords a very reliable indication of the occurrence of santalol in samples "C," "D," "E," "G" and "I," and the relative absence of this alcohol in samples "A," "B," "F" and "H." Sample "A," of course, is obtained from the wood of *Santalum lanceolatum,* and has been included merely for comparative purposes.

The specific gravities of the last-named sample are very low indeed, and are indicative of the occurrence of the secondary alcohol referred to in my Part I paper,

page 70. The boiling point as recorded therein is higher than the truth, and it will be corrected when its chemistry is published at a later date.

This particular alcohol has a specific gravity of about 0·938 to 0·940 and occurs in considerable amount in samples "B," "F," and more especially "H." It is proposed to investigate thoroughly this alcohol when a further consignment of the wood is made available.

I desire it to be clearly understood that the results given in Tables "A" and "B" do not refer to the commercial oil but to samples obtained from 1 cwt. lots of stickwood, roots and butts, furnished by the Conservator of Forests, and said by him to make on the whole a good representative sample of the Sandalwood as grown in the various parts of the State of Western Australia. A number of commercial samples of Western Australian Sandalwood oil have been examined since those published in 1928, and they reveal a marked improvement in the content of santalol (see *Chemist and Druggist,* 13th September, 1930).

In order that authentic data might be made available as to the source of the commercial oil, the manufacturers —Messrs. Plaimar Ltd., of Perth—kindly furnished, in April, 1932, 1 cwt. of butts of *Eucarya spicata.* This consignment was stated to represent a fair average sample of the wood used in the production of commercial Australian Sandalwood oil. The butts were reduced to as fine a condition as possible with the plant available and the essential oil produced therefrom by means of steam distillation. The oil thus obtained gave the following results on examination, *viz.*:

Specific gravity, $^{15}/_{15}°$, 0·9673.
Optical rotation, $-9{\cdot}6°$.
Refractive index, 20°, 1·5065.
Soluble in 2·0 vols. 70% alcohol (by weight).

Insoluble in 10 vols. 70% alcohol (by volume).
Ester No., 13·6.
Ester No. after acetylation, 182·6.
20 cc. oil yielded 5·0 grs. santalenic acid.

100 grs. of the crude oil were heated on a boiling water bath for 2 hours with 100 grs. each phthalic anhydride and benzene. 63% of alcohols was returned, which gave the following results on distillation, *viz.*:

Fraction.	Volume.	Boiling Point.	$d\frac{15^\circ}{15^\circ}$	$a_D^{20^\circ}$	$n_D^{20^\circ}$
1	8 cc.	145-148° (3 mm.)	0·9742	−5°	1·5072
2	48 cc.	149-152° (3 mm.)	0·9717	−9·0°	1·5088

FRACTION NO. 2.

Oxidation to Santalenic Acid.

20 cc. of this sample were oxidised with potassium permanganate in accordance with procedure described in *Journ. Roy. Soc. N.S.W.*, Vol. LXII (1928), page 68, when the high yield of 7 grammes crude santalenic acid was obtained. The crude acid after purification from dilute ethyl alcohol melted sharply at 76·5°.

Preparation of Allophanate.

The allophanate was prepared in good yield in accordance with the method described (*l.c.*). After purification from methyl alcohol it melted at 162-163° and was therefore identical with allophanate of β santalol.

Oxidation to Santalal.

5 cc. of the fraction were oxidised at room temperature (15° C.) with 50 cc. Beckman's chromic acid mixture. The crude santalal was removed by means of ether and treated with a solution of semicarbazide acetate in ethyl alcohol solution. The semicarbazone thus obtained after repeated recrystallisation from ethyl alcohol melted at 230°.

The good yields of the above mentioned characteristic derivatives, together with the high specific gravity of the alcoholic fractions, provides abundant evidence that santalol is present to the extent of about 90% in the alcoholic portion of the oil, equivalent to 56% in the crude oil.

Commercial oils purchased in the open market have been found to contain upwards of 60% santalol, computing the yield from the weight of crude santalenic acid yielded on oxidation of 20 cc. of the oil. A commercial sample of East Indian oil treated under similar conditions and at the same time gave 7·0 grammes crude santalenic acid.

The botanical nomenclature of Australian Sandalwood will be discussed in a subsequent communication. Meantime, whatever may be the outcome of the controversy which has raged around its botanical classification during the past five years, I am of the opinion that when once a specific name has been given to a plant which subsequently comes into commercial prominence, it is very unwise to alter it if it can reasonably be avoided.

In conclusion, I desire to express thanks to many persons for assisting in this investigation; Mr. F. R. Morrison, F.C.S., A.A.C.I., Assistant Economic Chemist, for his help in the chemical examination of the oils; Mr. S. L. Kessell, Conservator of Forests, Western Australia, for the excellent supply of wood upon which the investigation is based. I am also indebted to Mr. H. V. Marr, Managing Director, Messrs. Plaimar Ltd., Perth, for his interest in the investigation and for the supply of wood furnished in April, 1932, and to Mr. F. Matthews, of Messrs. Elliott Bros. Ltd., Sydney, for authentic samples of commercial Sandalwood oils.

TABLE "A."

Crude Oils obtained from Specimens of Sandalwood from Various Parts of Western Australia.

Sample.	Yield of Oil.	$d\frac{15°}{15°}$	$a_D^{20°}$	$n_D^{20°}$	Solubility in 70% Alcohol.		Ester No. 1½ hrs. Hot Sap.	Ester No. after Acetylation.	Origin of Wood Examined.
					By Volume.	By Weight.			
A	2·4%	0·9474	−58·6°	1·5072	Vols. 4·5	Vols. 1·7	8·5	199·5	*Santalum lanceolatum* from Derby (North-West).
B	1·5%	0·9489	− 6·2°	1·5025	6·5	1·6	12·3	178·0	*Eucarya spicata* stickwood from Kanowna district.
C	(1·6%) 2·4%	0·9606	− 6·0°	1·5044	3·8	1·5	12·0	195·0	*Eucarya spicata* roots and butts from Kanowna district.
D	1·5%	0·9559	+ 4·2°	1·5054	5·0	1·6	12·8	195·3	*Eucarya spicata* stickwood from near the coast, where the rainfall is better (Geraldton district).
E	2·4%	0·9645	− 4·0°	1·5056	4·0	1·5	8·7	199·3	*Eucarya spicata* roots and butts from Geraldton district.
F	1·3%	0·9514	−10·0°	1·5030	7·5	1·7	10·8	177·1	*Eucarya spicata* stickwood from rocky hills country (Kalgoorlie district).
G	2·6%	0·9633	− 4·0°	1·5057	7·0	1·7	10·0	194·0	*Eucarya spicata* roots and butts from rocky hills country (Kalgoorlie district).
H	1·4%	0·9454	−18·8°	1·5003	10·0	2·0	13·9	172·8	*Eucarya spicata* stickwood from rich flat country (Kalgoorlie district).
I	2·2%	0·9577	− 9·3°	1·5041	5·6	1·7	10·4	188·7	*Eucarya spicata* roots and butts from rich flat country (Kalgoorlie district).

TABLE "B."

The Alcoholic Constituents separated from the Crude Oils (Table "A") by means of Phthalic Anhydride.

Sample.	Weight of Alcohols Recovered from 100 grms. Crude Oil.	Distillation Range.	Volume.	$d\frac{15°}{15°}$	$a_D^{20°}$	$n_D^{20°}$	Weight of Santalenic Acid from 20 cc.	Weight and Melting Point of Allophanate. (From 10 cc.)	Remarks.
	grms.		cc.				grms.	grms.	
A	75	Below 150° at 2 mm. 150°–154° (2–3 mm.).	3 65	0·9489 0·9487	−62·0° −62·0°	1·5080 1·5094	— Nil.	4·2 108° (?)	From *Santalum lanceolatum.*
B	60	Below 150° at 3 mm. 150°–160° (3 mm.).	5 50	0·9441 0·9486	+ 2·2° − 1·1°	1·5030 1·5054	— Nil.	Nil.	From *Eucarya spicata* stickwood.
C	68	Below 151° at 2–3 mm. 151°–156° (2–3 mm.).	4 58	0·9600 0·9596	− 1·0° − 2·8°	1·5050 1·5065	— 2·5	2·0 155°–156°	From *Eucarya spicata* roots and butts.
D	56	Below 146° at 2–3 mm. 146°–154° (2–3 mm.).	5 49	0·9509 0·9506	+ 4·4° + 5·2°	1·5052 1·5070	— 2·0	1·0 152°	From *Eucarya spicata* stickwood.
E	67	Below 156° at 5 mm. 156°–160° (3–4 mm.).	3 55	0·9643 0·9655	− 3·6° − 5·2°	1·5060 1·5072	— 4·5	2·5 155°–156°	From *Eucarya spicata* roots and butts.
F	50	150°–159° (4 mm.). 160°–164° (4 mm.).	8 40	0·9449 0·9465	+ 0·1° − 0·65°	1·5036 1·5050	— Nil.	Nil.	From *Eucarya spicata* stickwood.
G	70	140°–149° (3 mm.). 150°–161° (3 mm.).	10 55	Lost. 0·9632	— − 2·5°	— 1·5071	— 3·3	2·0 155°–156°	From *Eucarya spicata* roots and butts.
H	44	Below 151° (4–5 mm.). 152°–161° (4–5 mm.).	5 34	0·9342 0·9439	− 0·6° − 3·5°	1·5011 1·5043	— Nil.	Nil.	From *Eucarya spicata* stickwood.
I	62	140°–148° (3 mm.). 148°–160° (3 mm.).	13 45	0·9311 0·9593	− 2·0° − 5·25°	1·5030 1·5073	— 2·0	1·2 155°–156°	From *Eucarya spicata* roots and butts.

RIPPLE-MARKS IN THE NARRABEEN SERIES ALONG THE COAST OF NEW SOUTH WALES.

By Alma G. Culey, B.Sc.,

Communicated by Professor L. A. Cotton.

(With Plate V and five text-figures.)

(*Read before the Royal Society of New South Wales, August 3, 1932.*)

The Narrabeen Series is the lower division of the Triassic System in New South Wales and overlies rocks of Kamilaroi Age; above, the Narrabeen beds pass into the middle division of the Triassic—the Hawkesbury Series.

The study of the ripple-marks in the Narrabeen Series was undertaken with the hope of gaining information as to their mode of origin.

Short Notes on the Formation and Interpretation of Ripple-marks.

A short description of the method of formation and interpretation of the main types of ripple-marks seems necessary at this stage. Reference for this has been made to papers by Kindle,[4] Bucher,[1] Hunt,[2] Twenhofel.[5]

Fossil ripple-marks are exposed on the surface of some sedimentary rocks. They are marks or corrugations which suggest water ripples and are formed by water or wind action at the time of deposition of the sedimentary rocks.

Ripple-marks can be classified into three main types, (*a*) wave ripple, (*b*) water-current ripple, (*c*) wind-current ripple. Complex ripple-marks are variations of one or more of the above.

Wave ripples may be formed on the floor of a body of water which is tideless and also free from currents. Such a body may be a lake or an arm of the sea cut off from the main ocean. Wind blowing over the water surface produces an orbital motion of the water particles. This motion is circular in deep water but grades through elliptical motion to an almost horizontal to-and-fro oscillation in shallow water. Where the water is sufficiently shallow the movement of the water particles induces a corresponding oscillation in the loose sediment beneath. The continued motion causes a series of parallel ridges to be built up, their distances apart being proportional to the major axes of the oscillation ellipses. The production of vortices on either side of the ridges gives them a symmetrical profile with sharp crests and rounded troughs. Occasionally the crests may be rounded.

The direction of the ripples, then, is dependent on the direction of the wind, but in shallow water there is a tendency for the waves to wheel round parallel to the contour lines of the bottom, and thus the ridges become approximately parallel to the shore-line, no matter what the direction of fetch of the wind.

Considerable confusion exists as regards nomenclature in the study of ripple-marks. In this paper the spacing of the ridges will be termed the wave length, and the height from trough to crest the amplitude.

The actual effect which depth of water and wave amplitude have on the wave length and amplitude of the ripple-marks has not yet been ascertained, but Kindle,

from observations made on the shore of Lake Ontario, gives us the following table:

Depth of Water.		Wave Length of Ripple-marks.
6 inches	.. .. ..	1 – 2 inches
$1\frac{1}{4}$ feet	.. .. ..	2 – 4 ,,
$2\frac{1}{2}$,,	.. .. ..	$3\frac{1}{2}$– 4 ,,
10 ,,	.. .. ..	4 – 6 ,,
11 ,,	.. .. ..	$4\frac{1}{2}$,,
20 ,,	.. .. ..	4 – 5 ,,

Also, he states that to his knowledge ripple-marks with a wave length of less than two inches are formed only in water having a depth of less than one foot.

Bucher[(1)] (p. 188) reports that Forel has conclusively shown that wave length diminishes with increasing depth of water; Kindle's observations for shallow water are contrary to this.

The relationship of depth of water to wave length may be summarised: (*a*) For shallow depths, as given in Kindle's table, there appears to be an increase of wave length with increase of depth. (*b*) "For moderate depths the size of the ripples is not very sensitive to variation of water depth." (*c*) For greater depths there is a decrease of wave length to a very small size.

Kindle refutes the idea fairly commonly accepted, that ripple-mark of any dimension, in itself, is sufficient criterion for shallow water deposition. He gives examples of ripple-mark produced at great depths.

Current Ripple-mark.—The continued flow of a current (water or air) over loose sediment is likely to set up ripple-marks, the ridges being at right angles to the direction of the current. Both water and wind ripple-marks have characteristic asymmetric profiles with a gentle stoss-side and a steep lee-side. Water-current ripples are formed along shores with a coastal current,

in water bodies under tidal influence, and as local occurrences in fresh-water lacustrine sediments.

According to Bucher, *cross ripples* are formed when one set of ripples intersects a previously formed set. The component ripples may be either symmetrical or asymmetrical. There are two classes of cross ripples—hexagonal, when the crests of the two sets of ripples intersect at an angle less than 90°, and rectangular, when they intersect at 90°. Accepting Bucher's theory of their formation, cross ripples can form anywhere where conditions are favourable for the formation of simple ripple-mark; but Kindle's theory demands very shallow water, and a barrier to set up the component systems.

Method of Measurement.

A very satisfactory and quick method of measurement of ripple-marks was suggested by Professor L. A. Cotton, M.A., D.Sc.

An ordinary pantograph was adapted (Fig. 1). The pantograph was attached by means of the screw "A" to

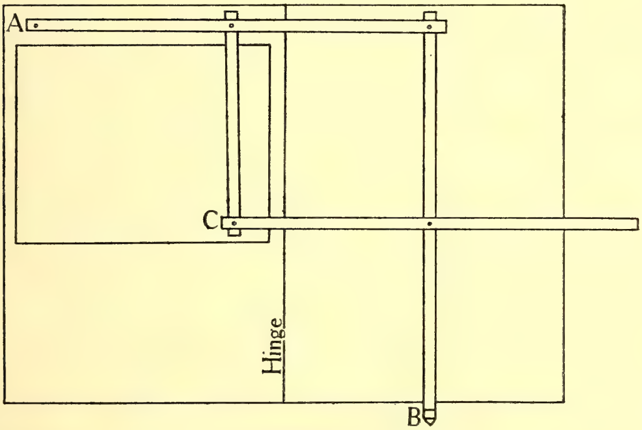

Figure 1.

a light board. The board was of 3-ply wood, and in order to make it more convenient for carrying, it was cut along a central line and hinged so that it could be folded into a convenient size. The usual tracer was replaced by a hard metal point "B," which could be drawn over the surface of the rock. To obtain traces of the profiles of the ripple-marks, the board was held vertically at right angles to the direction of the crests of the ripples, the tracer was drawn over the rock surface, and the pencil "C" traced the profile of the rippled surface on paper pinned on the board.

With the pantograph thus altered, only reduced drawings could be made. There was no necessity for varying the amount of reduction, so to facilitate comparison of ripple forms, all the measurements were done to half-scale.

The symmetry of the profiles obtained is sufficient to show whether they are formed by wave action, water current, or air current.

The directions of the ripple crests were measured by the compass of a clinometer rule. In the case of curved ripples, the direction tangential to the curves was read. The rule of the clinometer was used in measuring the wave length and amplitude of ripples in weathered exposures.

The ripple index, (the ratio $\frac{\text{wave length}}{\text{amplitude}}$), was calculated for all the measured ripple-marks, and was useful in comparison of forms.

Measurement of Ripple-marks in the Narrabeen Series.

The headlands of the coast between Pelican Point (7 miles north of The Entrance, Tuggerah) and Long Reef,

and also the coastal exposures between Garie and Stanwell Park, were examined for ripple-mark.

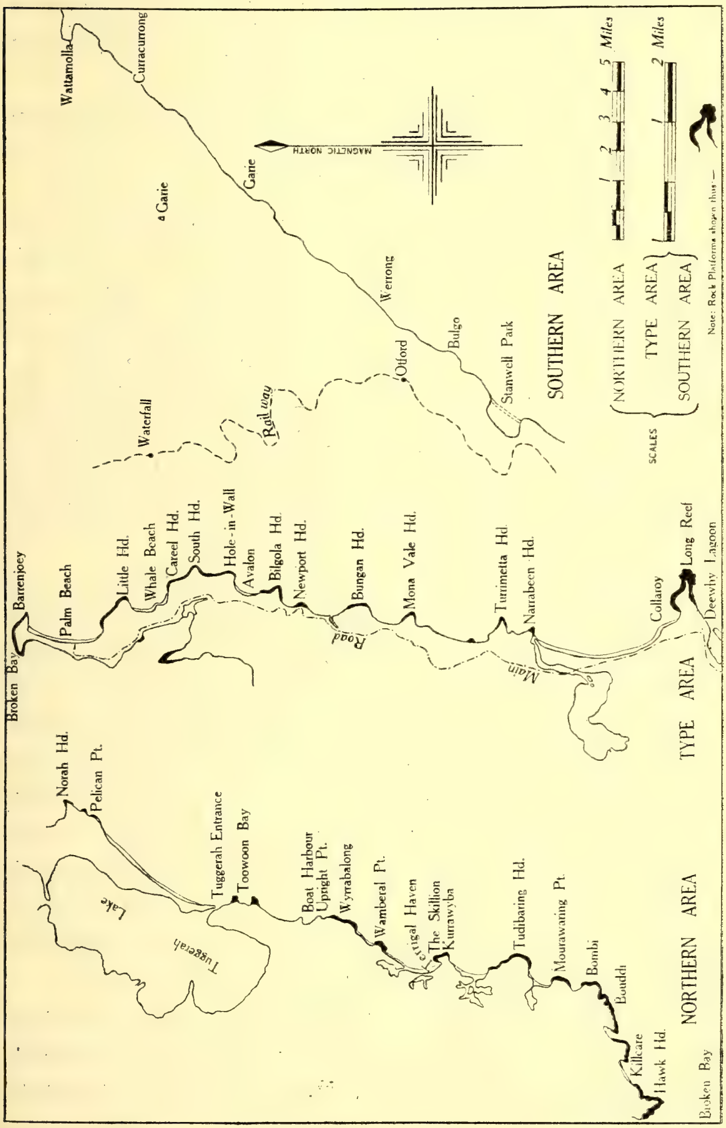

Figure 2.—Locality Map.

The work will be dealt with in three sections:

1. The area between Long Reef and Barrenjoey, being the type area for the Narrabeen beds.
2. The northern area between Broken Bay and Pelican Point.
3. The southern area between Garie and Stanwell Park.

1. (*a*) *General Geology of the Type Area.*

The rocks exposed in the cliff sections and rock platforms between Long Reef and Barrenjoey are upper Narrabeen beds, and are confined between the top chocolate shale horizon of the Narrabeen Series and the Hawkesbury sandstones. These beds comprise grey tuffs associated with the chocolate shales, overlain by rapidly alternating shales, sandstones, and intermediate types, these alternating beds being capped in some headlands by Hawkesbury sandstone.

The Narrabeen Series in this area has suffered gentle folding. The section between Narrabeen Head and Barrenjoey is really an anticline, with the axis passing through or near Bungan Head in a general E-W direction.

The cliff section at Bungan Head shows chocolate shale extending up the cliff face for approximately twenty feet. The rock platform at Mona Vale Head, south of Bungan Head, is of chocolate shale. The northern cliffs of this headland show chocolate shale to a height of about twelve feet; on the south side the top of the chocolate shale is a few feet above the platform level, and grey tuffs overlie the chocolate shale.

Newport Head, north of Bungan Head, has a chocolate shale platform, and thus corresponds to Mona Vale Head.

Turrimetta Head, south of Mona Vale, has chocolate shales with associated grey tuffs on the platform on the

northern side, but these give place to interbedded sandstone and shales on the southern side. This headland corresponds to Bilgola Head on the northern arm of the anticline.

The southern platform at Bilgola Head is chocolate shale (rising slightly higher than at Newport); the northern platform is interbedded shales and sandstones.

Narrabeen headland corresponds with the "Hole in the Wall" headland and South Head.

1. (*b*) *Measurement of Ripple-marks in the Type Area.*

Ripple-mark exposures were found *in situ* at Collaroy, Narrabeen Head, Turrimetta Head, "Hole in the Wall" Head, South Head, Little Head, and Barrenjoey. Over forty profiles altogether were taken of ripple-marks in this section, but over eighty different horizons were recorded and some measurements taken.

Several small exposures of ripple-mark may be seen at Collaroy. Those on the platform are preserved in a fine sandstone, and several horizons are ripple-marked. The wave length of these ripples averages one inch, and the directions vary. In the cliff section at the hydration anticline there are several small exposures in medium-grained sandstone. Their symmetry is definitely that of oscillation ripples. The wave length varied from 2–3 inches, ripple index from 6–12, and the directions from N 20° W, to E-W.

Narrabeen Head shows very many horizons of ripple-mark in the alternating shales and sandstones. The rock platform has four horizons in a vertical interval of four inches. An exposure at beach level, with an area of 42 feet by 37·5 feet, shows eight different sets of ripples in only eight inches vertically. Various exposures of

ripple-mark are found in grey shales and fine sandstones in the cliff ledges.

The directions range over a very wide angle, but in the cliff exposures there is a progressive change in a W-E direction from N 51° W to N 55° E.

Three sets of cross ripples are present—one in the rock-platform and the others in the exposure at sand-level. The direction of the sharper component in one case is the same as that of the simple ripples two inches below, and in a second instance, the same as simple ripples on the same horizon. This appears to be in favour of Bucher's theory that cross ripples are formed by one set of ripples interfering with a previously formed set, and not simultaneously by component current systems as suggested by Kindle. The directions of the stronger components are N 55° W, N 58° W, and N 32° W.

The ripples at Narrabeen Head are all of the oscillation type, with the exception of one set, which is asymmetric. The wave length averages 2·35 inches, with minimum and maximum limits of 1·7 inches and 3·4 inches, and the ripple index varies between ·9 and 15, the higher values generally obtaining for the finer sandstones and shales.

About one chain beyond Narrabeen Head, on Turrimetta beach, some grey sandstone ledges show ripple-marks of wave length 2 inches and 2·9 inches. Although these are separated by one foot vertically, they trend in the same direction, *viz.*, E-W, indicating stable conditions of sedimentation between these two horizons.

At the most southerly point on the Turrimetta Head platform cross ripples occur in a fine shaly sandstone. The strongest set of ripples trend N 20° W, and have a wave length of 3·5 inches approximately. The weaker

ripples have a wave length of 4 to 4·5 inches. Both sets are wave formed. No other ripples observed on Turrimetta were *in situ,* but two boulders showed asymmetrical ripple-marks, both in shale, and having values of 15 and 18 for the ripple index. The other ripples are all of the oscillation type, and one boulder with three layers of ripple-marks, shows a progressive change in direction. Two sets of ripples in sandstone have wave lengths of 3·5 inches and 3·6 inches, which is much greater than the average of 2·28 inches. Many of the ripples are in close association with abundant fossil worm burrows.

At the headland north of Mona Vale beach no ripples were found *in situ,* but several rippled boulders of sandstone had fallen from above the chocolate shales which formed the platforms and the lower portion of the cliff. One was particularly interesting in showing intimate association of ripple-marks with *Phyllotheca.* A stem of *Phyllotheca,* about five-eighths of an inch wide, has been preserved lying on the rippled surface, making an angle of almost ninety degrees with the ripple crests. The wave length of the ripples is 1·5 inches, and the amplitude 0·15 inch, and the fact that the *Phyllotheca* stem has produced no noticeable distortion of the ripple forms, testifies to the flexibility of the plant stem.

Oscillation ripples are found in grey shale and sandstone boulders at Bungan Head.

Ripple-marked boulders are present at Newport. The sandstones show ripple-mark of greater wave length than usual, ranging from 2·6 inches to a maximum of 4·5 inches. A grey shale boulder, besides being rippled, contains abundant plant fossils (mainly *Phyllotheca*), and also has worm-burrows on the same surface as the ripples.

From south to north round Bilgola Head, the chocolate shales give place to fine sandstones and sandy shales. It is in this horizon, on the northern platform, that abundant ripple-marks occur. The rocks are finely laminated, and in a vertical interval of only a few inches ripple-mark directions N 8° W, N 13° W, N 20° E, N 70° E, N 64° E, N 70° E, and N 75° E were measured. The wave length averages one inch, but reaches a maximum of two inches.

Ripple exposures are found *in situ* and in boulders at the "Hole in the Wall" rock platform. Both simple and cross ripples occur. The best defined set in the cross ripples trends in a direction N 70° W, the other set almost at right angles to this. The wave length of the ripples varies vetween 2 inches and 3·5 inches, and the direction between N 40° W and N 40° E.

The rock ledges at the base of the cliffs between South Head and the "Hole in the Wall" show an astonishing number of ripple-marked horizons. In a vertical interval of three feet nine inches eighteen different horizons were noted. The ripple-marks occur in very rapidly alternating beds of very fine sandstone, sandy shales, or finer shales. Almost all the sandy material is rippled and the directions are variable, although some ripples, trending E-W, are superimposed throughout a few inches. While the ripples vary greatly in size, they are all of the oscillation type. It is in a sandstone boulder from here that the ripples occur which have the maximum wave length observed, *viz.*, 5·2 inches.

The only other ripple-mark exposures in this section are two small isolated exposures. The first is in sandstone which forms the headland south of Palm Beach. Indications of ripple-marks are seen in the cliff faces above this sandstone. The second is at the eastern

point of Barrenjoey. The exposure is small, and in massive sandstone. Again, indications of ripple-marks can be seen in the sandy shales in the cliff face.

2. *(a) General Geology of the Northern Area.*

Between the Hawkesbury River and Pelican Point we have the entire sequence of the Narrabeen Series from the Hawkesbury sandstones to the base, overlying conglomerates at the top of the Kamilaroi system.

The headlands between Terrigal and Killcare expose the same sequence as between Narrabeen and Barrenjoey. The general nature of the Killcare rocks is very similar to those at and near South Head.

To the north, Wamberal headland gives the first exposure of the upper chocolate shales, which are associated with grey tuffs and grey shales.

The southern portion of Wyrrabalong rock-platform consists of a fine tuffaceous sandstone, greenish grey in colour. This is in part weathered brown, the resultant rock looking very like the chocolate shales but being more sandy in character. These beds, dipping S 24° W at about 5°, are finely bedded, and form a very level platform, eroded edges showing at intervals. The chocolate shales outcrop at beach level and at the base of the cliff on the southern side of Wyrrabalong. The northerly cliff section of Wyrrabalong exposes a much greater thickness of chocolate shales. A rough estimate was made of one hundred feet of chocolate shales with subordinate greenish sandy tuff interbedded, these being overlain by approximately one hundred feet of a flaggy tuffaceous sandstone. The chocolate shales are covered with grass as is often the case with chocolate shale cliffs.

There are two bands of chocolate shale exposed at Point Upright, one at reef-level, the other about nine feet

up the cliff, separated from the lower by tuffaceous sandstone.

The small headland north of Boat Harbour shows weathered exposures of chocolate shales. The lower shales are not typical chocolate shales, but their sandy nature is no doubt due to their being near the edge of the basin of deposition. They are associated with green tuff and one sedimentary type grades into the other. These are separated from the upper band by about twelve feet of sandstone.

The most northerly coastal exposure of chocolate shales is found at Toowoon Bay, where a vertical thickness of ten feet was estimated. This is underlain by massive tuffaceous sandstone and conglomerate which lie near the base of the Narrabeen Series.

The beds in the northern area have a general gentle southerly dip, and no definite folding is apparent.

2. (*b*) *Measurement of Ripple-marks in the Northern Area.*

The rock platform south of Killcare exposes shaly sandstones (purplish in colour), similar in appearance to those of Narrabeen Head. The alternating beds in the cliff section are capped by Hawkesbury sandstone. The platform has many ripple-mark exposures, but all are badly weathered, and only the crests remain in many cases. The wave length averages between 1 inch and 2 inches, and direction readings are varied for the ripples at different horizons. One set of cross ripples has components N 10° W and N 78° E.

The stretch of coast between Killcare and Mourawaring Point is inaccessible.

Mourawaring Point shows numerous weathered ripples in the fine sediments exposed. The wave length of the

ripples averages 1·5 inches, few being only 1 inch, and others reaching a maximum of 2 inches. In a vertical interval of about four feet fairly good exposures were noted in sixteen different horizons, the directions varying between N 70° W and N 53° E.

Tudibaring Head, north of Tudibaring beach, exposes more sandstone than the more southerly headlands, and in this the ripple-marks are more rare and very badly preserved. Only a few very poor exposures were observed, and directions noted were N 7° E and N 85° E.

Sandstones are again more prominent in the headland south of Avoca, and no ripple-marks were found in these.

On the northern platform of the Skillion, Terrigal, a few exposures of ripple-marks occur. One set of markings, having a wave length of 1·5 inches, and a direction of N 34° E, is persistent over two inches vertically, and in a slightly lower horizon other ripples occur trending N 40° E, indicating constant conditions of ripple formation over a time sufficient for the consolidation of the lower ripples, and subsequent deposition of sediment.

But it is on the southern side of the Skillion towards Kurrawyba Head, that some excellent exposures occur. Many of these are very well preserved. The average direction readings on twenty-five different exposures is N 30° E, the limiting readings being N 25° W and N 84° E. The average wave length is about 1 inch, and ripples were recorded from here with wave lengths of only 0·5 inch and 0·7 inch, each being in fine sediment. The component directions of a cross ripple exposure are N 15° E and N 62° W.

Proceeding south from the Skillion the alternating shale and sandstone give way to more massive sandstone ledges which are practically free of ripples, but those which do occur have a wave length of 3–3·3 inches. Also,

in this sandstone, interference ripple-marks of large size and irregular pattern can be seen. They are similar to those formed in water bodies under the influence of current action.

Ripple-marks were not observed at Wamberal Point, but many were found on the rock platform at Wyrrabalong. Here greenish grey tuffs form the platform, and these are intimately associated with chocolate shales. On the platform are many exposures, but most of the platform is covered with algæ, leaving only a few rocks exposed. The directions are variable, mostly being between the limits N 35° W and N 24° E. The wave length averages one inch, and the limits observed were 0·8 inch and 1·05 inches.

The chocolate shale at Wyrrabalong is interbedded in narrow bands of eight inches or less with green tuffs. In several instances these interbedded tuffs are rippled. Specially interesting is a junction surface between tuff and chocolate shale, where the shale rests on the rippled tuff surface.

Also, in this tuff are irregular interference ripples similar to those at Kurrawyba, and evidently due to some current or tidal action. Worm burrows and sun cracks are found in the tuff close by these ripples.

Only two other exposures of ripple-marks are noted and these are on the small rock platform north of Boat Harbour. In some sandy chocolate shale some shallow ripple-marks of wave length 1·3 inches occur. These are particularly interesting in being the lowest observed in the series—being at the base of the lower chocolate shales.

3. *The Southern Section.*

The headland north of Garie Beach exposes the upper chocolate shale horizon, which has here a thickness of

about forty-five feet, overlain by alternating grey shales and sandstone. Below are shales and sandstones and about one hundred and fifty feet lower than the chocolate shales is a horizon of cupiferous basic tuff.

Much of the coast is inaccessible south of Garie, with truncated headlands covered with vegetation and comparatively few rock platforms.

A little south of Otford rock platforms are developed, but there the rock formation is coarse sandstone and conglomerate, forming the lower beds of the Narrabeen Series. The upper chocolate shales are exposed at Otford, and the cliffs between here and Stanwell Park would, if not covered so heavily with vegetation, show the sequence between the top chocolate shales and the base of the Narrabeen Series. No detailed work could be done in this section.

The rock platforms, being of coarse sediment, do not show any ripple-mark.

In fact, no ripple-marks were found by the writer, in the southern section of the Narrabeen Series, other than at Waterfall. The ripples here are exposed in the cliff section and on fallen boulders at the Lower Falls, two miles along the Lady Carrington Drive from Waterfall. Here, in the cliff face, Narrabeen grey shales with abundant *Phyllotheca,* and fine sandstones are exposed, overlain by more massive coarse Hawkesbury sandstone. Boulders show weathered ripple-marks with a wave length of about one inch. Some grey shale shows ripple-mark of wave length three inches. The ripples are symmetrical and therefore wave formed; and the upper ones are only fifteen inches below the Narrabeen-Hawkesbury junction.

Reference has been made in *N.S.W. Geol. Surv. Mem.,* 7, to ripple-marks in the Corrimal-Balgownie colliery,

formed in a horizon two feet six inches above the coal, and to a rippled horizon between Bellambi and Mount Keira. But "Palæontological evidence available does not permit of a definite age being assigned to this horizon, and it may be either early Triassic or late Permo-Carboniferous."

Summary of Data Acquired.

From information now available the facts may be listed as follows:

1. Ripple-marks are developed in the Narrabeen beds at various levels in the series.
2. The lowest ripple-marks noted are at the base of the chocolate shales, north of Boat Harbour. Only a few exposures were observed at, and near, this level.
3. More numerous exposures were found in the tuffs associated with the chocolate shales, higher in the series, at Wyrrabalong.
4. The ripples are best developed in the alternating shale and sandstone formation between the upper chocolate shales and the massive Hawkesbury sandstone. The individual beds vary from as little as $\frac{1}{8}$ inch to several feet, many of the beds being 1 foot or less in thickness. One bed may grade into another, and they are not persistent. Apparently most of the individual beds are ripple-marked.
5. From these facts one sees that the ripples are not confined to a narrow limit in the Narrabeen beds, but are developed over quite a large vertical range, from at least the base of the lower chocolate shales (north of Boat Harbour), to within

15 inches of the Hawkesbury sandstone (as seen at Waterfall).

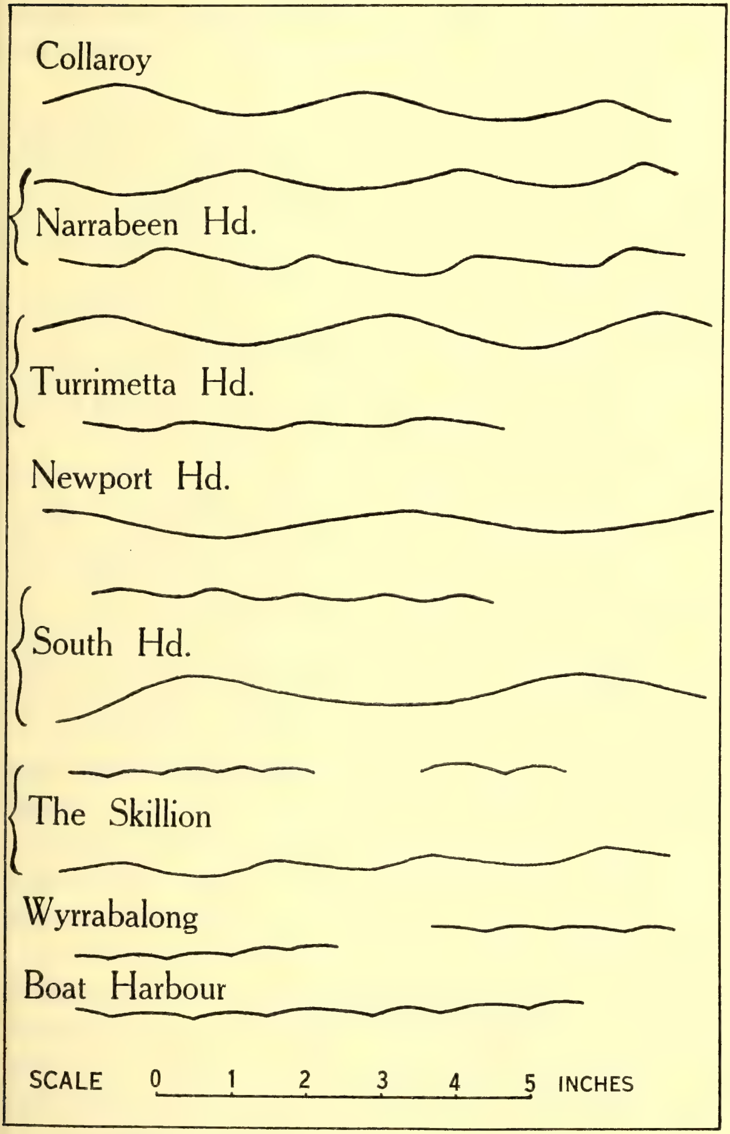

Fig. 3.—Selected profiles of ripple-marks.

6. The rippled beds extend from near Boat Harbour to Collaroy, a distance of about thirty miles along the coast. An isolated exposure of ripples was noted at Waterfall, twenty-four miles south of Sydney.
7. From the profiles drawn, it is seen that the ripple-marks are all of the oscillation (wave) type, with the exceptions of one at Narrabeen, two at Turrimetta, and irregular interference ripples at Wyrrabalong and Kurrawyba.

   Generally, the rippled shales show a wave length of about two inches—they are shallow, the crests usually being well marked and angular. The ripple index is high, usually between 14 and 20.

   The wave lengths of the ripples in the sandy sediments vary from 0·5 inch up to 5·2 inches as a maximum. The ripples of very small wave length ($\leqq$ 1 inch) were very rare. Only one specimen was seen with ripple-mark of wave length 5·2 inches, and only two specimens of wave length 4·5 inches. The majority of ripple-marks have a wave length between 1 and 3 inches.

   The ripple indices for the sandy shales and sandstones are usually lower than for the shales, having values near 10 or 12.
8. The directions of trend of the ripple-marks, though apparently varied, are significant. This will be discussed later.
9. Six exposures of cross ripples have been examined. The strongest sets trended in the following directions: N 55° W, N 58° W, N 32° W (Narrabeen), N 20° W (Turrimetta), N 70° W (Hole in the Wall). In the case of the cross ripples at

the Skillion, the two component directions seemed to be equally marked, and of these directions one was N 62° W.

10. (*a*) Ripple-marked beds are closely associated with sun-cracks at Collaroy, Narrabeen, Turrimetta, South Head, Kurrawyba Head, and Wyrrabalong.

(*b*) Horizons of worm burrows are found in layers interbedded with ripple-marked beds. In several cases worm burrows were found on the same surface as ripples, *e.g.*, in grey shale at Newport, and sandstone at Kurrawyba Head. A specimen from Narrabeen Head shows vertical burrows cutting up through the ripples.

(*c*) Shales with abundant plant remains are intimately associated with ripple-marks. A specimen from Mona Vale shows *Phyllotheca* on the same surface as ripple-marks.

Conclusions.

The presence of oscillation ripple-marks necessitates a body of water free from current or tidal action. Such a body of water must be either a fresh-water lake or a body of marine water cut off from tidal influence. The very close association of the ripple-marks with plant remains certainly indicates fresh-water conditions. So one may conclude that the sediments were deposited in a fresh-water lake.

But there are some asymmetric ripples to account for. Kindle(4) (p. 12), quotes 6·3 and 4 as the ripple indices for two sets of water-current ripples in the St. Lawrence, and 24 and 25 as indices for wind-formed ripples at Wellington—"Thus showing an index number four to six times greater than that of the water-made ripple-marks."

The indices (15, 18, 19) of the measured marks at Narrabeen and Turrimetta indicate wind agency. This is quite possible, for a shallow lake could easily be drained in part and wind ripples could then develop. Even if the inference from the ripple indices is not correct, and the ripples are water formed, there is no need to postulate other than lacustrine conditions. A local disturbance (*e.g.*, a storm), or local features (*e.g.*, a stream flowing into a lake), may produce local currents which may leave their record in fossil asymmetric ripple-marks. The irregular interference ripples at Wyrrabalong and Kurrawyba are undoubtedly water formed.

The presence of ripple-marks at intervals between the lower and upper chocolate shale horizons indicates shallow water conditions of deposition at these intervals. Ripples were not noticed in these sufficient to establish a conclusion that there was continuous shallow water sedimentation, but it can be seen that even if such conditions were not continuous, there was repeated occurrence of shallow water conditions. The presence of ripple-marks in the tuffs interbedded with the chocolate shales would suggest shallow water deposition of the latter.

The ripple-marks occur so abundantly in so many horizons in the upper Narrabeen beds between the upper chocolate shales and the Hawkesbury sandstones that it seems quite reasonable to assume shallow conditions during the whole period of accumulation of these alternating beds.

From a number of observations Kindle[4] (p. 29) concluded that:

(1) Ripple-marks with a wave length less than two inches formed only in water having a depth of less than one foot.

(2) Ripples of wave length between one and two inches were common in water six inches deep.

(3) Ripples of wave length between three and a half inches and six inches formed in water of depth about ten feet.

All the ripples of the Narrabeen Series, therefore, are likely to have formed in water the depth of which could vary between a few inches and about ten feet, although there is a possibility of some of the ripples having formed at a greater depth.

The presence of sun-cracks and the wind-formed ripple-marks would indicate temporary exposure above water level at times. Worm-burrows require shallow water, as do terrestrial plants.

The Significance of the Directions of the Ripple-marks.

The directions of trend of the ripple-marks are apparently varied, but on plotting them for the Type and Northern Areas separately definite groupings can be seen. The numbers of ripple directions clustering about the N-S, NE-SW, E-W, and SE-NW lines, respectively, were counted, reduced to percentages, and plotted as in Figs. 4 and 5.

Similarly, a diagram (Fig. 4) was drawn showing quantitatively, in time, the wind directions at Sydney (Type Area), for the past twenty years. Winds from opposite points of the compass form symmetrical wave-ripples trending in the one direction at right angles to the directions of the winds, *e.g.,* ripple-marks trending N-S are formed by winds either from the east or west. Therefore the duration in hours of the winds from opposite points were added and plotted as a percentage of the total wind duration along the corresponding direction for the ripples. A very striking similarity was

noticed between the ripple diagram and wind diagram for the Type Area. This suggests that the planetary wind systems of lower Triassic time were the same as those prevailing at the present time in this area.

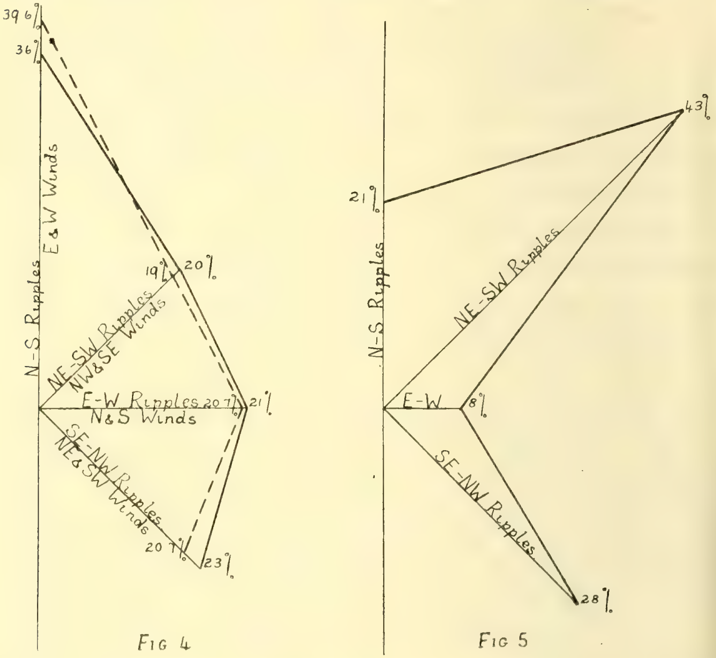

Fig. 4.—The diagram drawn with the heavy line is the ripple mark diagram for the Type Area. It is based on 66 measured directions. The diagram drawn with the broken line is the wind diagram for the Type Area (Sydney), based on the records for the years 1911-1930.

Fig. 5.—Ripple-mark diagram for the Northern Area, based on 45 measured directions.

The figure (Fig. 5) drawn for ripples in the Northern Area was of a different character, and unfortunately quantitative observations for the wind systems were not available for a comparison diagram. However, comparison of general observations of the prevailing winds at Sydney and Newcastle shows a marked dissimilarity

in the summer winds. The area in question lies approximately half-way between Sydney and Newcastle. At Sydney the prevailing directions are east and north-east, while at Newcastle the south winds are predominant. So, although from this diagram one has nothing to add in support of conclusions formed from the study of diagrams for the Type Area, the different nature of the ripple diagram cannot be taken as evidence against similar planetary wind systems. The difference could probably be explained by the change of wind systems with change of locality.

From the conclusion that the planetary winds of early Triassic and the present time, are the same, one may deduce that the poles were in the same position then as now. Since the Type Area is in the anticyclone belt, a critical position, a movement of the pole of only a few degrees would probably result in a marked change of wind direction, as from the SE Trades to the Roaring Forties, or *vice versa*. This eliminates the possibility of any notable difference of the position of the pole in Triassic times.

In the case of the cross ripples it is noticed that the directions of the strongest ripples are confined between N 20° W and N 70° W. The strongest ripples are formed by the strongest waves, usually, and the strength of the wave is influenced by the shape of the lake, or by the distance of fetch. It seems possible that these directions indicate the direction of greatest fetch, which would be between N 20° E and N 70° E. This would mean that the lake would be elongated in a NE-SW direction.

Concluding, one may imagine the Triassic Narrabeen Lake as a shallow, subsiding, fresh-water lake, probably elongated in a NE-SW direction. Surrounding it one would see areas of low relief from which the sediments

are brought down and deposited quietly in the lake, the prevailing calm being interrupted by local disturbances and ejections of tuffs, followed again by quiet sedimentation.

Finally, the writer would like to thank those who have helped with this paper; particularly Professor L. A. Cotton, M.A., D.Sc., for many helpful suggestions, and also Mr. D. J. Mares, of the Meteorological Bureau, Sydney, for making available wind data of Newcastle.

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Fig. 1.

Fig. 2.

Fig. 1.—Ripple-marks on the platform at Narrabeen Head.

Fig. 2.—Boulder showing two directions of ripple-marks, Bilgola Head.

DERIVATIVES OF 2-PHENYL QUINOLINE.

Part I.

PREPARATION OF SOME "ATOPHANS" FROM VERATRIC ALDEHYDE.

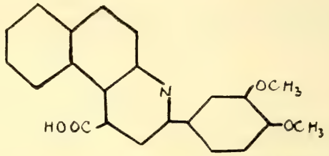
By Muriel Gertrude Holdsworth, M.Sc.,
and Francis Lions, B.Sc., Ph.D.

(Read before the Royal Society of New South Wales, August 3, 1932.)

Döbner's quinoline synthesis (*cf. Berichte* (1887), **20**, 277)—condensation of an aromatic amine with pyruvic acid and an aldehyde to a cinchoninic acid—has frequently been used for the characterisation of aldehydes. The reaction is very general, but in particular, Döbner has shown that β-naphthylamine exhibits a special facility for quinoline formation with any aldehyde (except α-hydroxy aldehydes) and any pyruvic acid (*Berichte* (1894), **27**, 2020), though Johnson and Adams (*J.A.C.S.* (1923), **44**, 1571) have since shown the synthesis to be less general for aliphatic than for aromatic aldehydes.

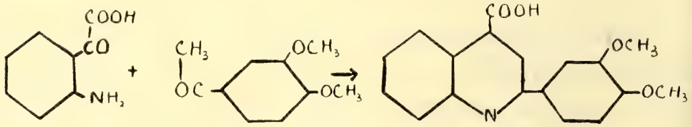
Apparently, up to the present, veratric aldehyde—3 : 4-dimethoxybenzaldehyde—has not been used in syntheses of the Döbner type. It has now been shown that this aldehyde condenses quite readily with pyruvic acid and various aromatic amines in alcoholic solution to give the corresponding 2-veratryl cinchoninic acids. Thus β-naphthylamine added to a boiling alcoholic solution of veratric aldehyde and pyruvic acid rapidly condenses to

the "β-naphthocinchoninic acid," 2-veratryl-5:6-benzo-quinoline-4-carboxylic acid (I).



I

In the same way aniline gives 2-veratryl-quinoline-4-carboxylic acid (II), which has also been obtained by Pfitzinger's method—by condensation of acetoveratrone with isatic acid in strongly alkaline alcoholic solution.

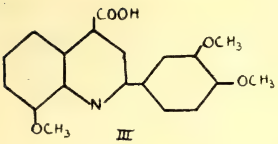


II

Condensation of veratric aldehyde and pyruvic acid with o-anisidine, m-anisidine, p-anisidine, m-aminophenol and p-aminophenol respectively leads to the formation of 2-veratryl-8-methoxy-quinoline-4-carboxylic acid (III), 2-veratryl-7-methoxy-quinoline-4-carboxylic acid (IV), 2-veratryl-6-methoxy-quinoline-4-carboxylic acid (V), 2-veratryl-7-hydroxy-quinoline-4-carboxylic acid (VI), and 2-veratryl-6-hydroxy-quinoline-4-carboxylic acid (VII), respectively; but no quinoline derivative was obtained from o-aminophenol.

Further, condensation of veratric aldehyde with m-dimethylamino-aniline and pyruvic acid in alcoholic solution leads to formation of 2-veratryl-7-dimethylamino-quinoline-4-carboxylic acid (VIII).

If the aromatic amine used is m-phenylene diamine a double quinoline ring closure occurs and $\alpha:\alpha^1$-diveratryl



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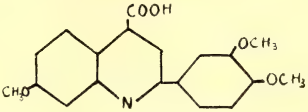

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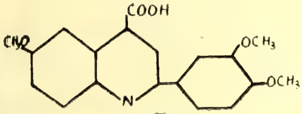

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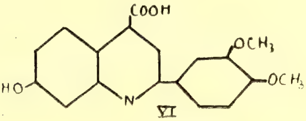

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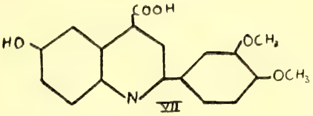
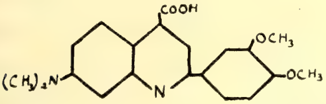
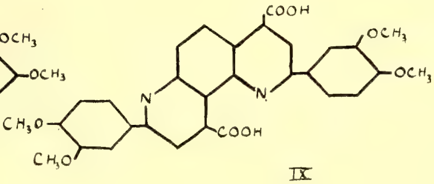


VII

phenanthroline-$\gamma:\gamma^1$-dicarboxylic acid (IX) is obtained in good yield.



VIII



IX

Experimental.

2-Veratryl-5:6-benzoquinoline-4-carboxylic acid (I).

A solution of β-naphthylamine (5 g.) in alcohol (20 cc.) was added gradually to a solution of veratric aldehyde (5 g.) and pyruvic acid (3 g.) in boiling alcohol (50 cc.). The β-naphthocinchoninic acid came down almost immediately in pale yellow crystals. After heating on the water-bath for half an hour, the solution was cooled and filtered. The precipitated acid was washed with alcohol and ether. Yield 10 grams. Recrystallised from boiling alcohol it melted at 142–143° C.

(Found, C = 73·3, H = 5·4%; calculated for $C_{22}H_{17}O_4N$, C = 73·5, H = 4·8%.) The substance is only sparingly soluble in all the usual organic solvents—as indeed are all the other "atophans" described below.

2-Veratryl-quinoline-4-carboxylic acid (II).

(*a*) A solution of aniline (10·5 g.) in alcohol (50 cc.) was added gradually to a solution of veratric aldehyde (17 g.) and pyruvic acid (10 g.) in boiling alcohol (150 cc.). After refluxing for two hours, most of the alcohol was removed, when the acid crystallised out. Yield 10·5 grams (32% of theory). It was recrystallised from boiling alcohol in which it is only sparingly soluble and thus obtained in fine yellow needles melting at 235° C. (Found, C = 69·7, H = 5·1%; calculated for $C_{18}H_{15}O_4N$, C = 69·9, H = 4·9%.)

(*b*) A solution of isatin (15 g.) in 30% alcoholic caustic potash (60 cc.) with acetoveratrone (15 g.) was refluxed for 8 hours. The alcohol was then removed and the product obtained by acidifying with dilute acetic acid. Yield 22 g. (85% of theory). Purified as before by recrystallisation from boiling alcohol, it melted at 235° C., alone or mixed with a specimen obtained as above.

2-Veratryl-8-methoxyquinoline-4-carboxylic acid (III).

Obtained by refluxing a solution of o-anisidine (3·5 g.), veratric aldehyde (5 g.) and pyruvic acid (3 g.) in alcohol (50 cc.) for some hours and then allowing to stand overnight, this cinchoninic acid came down as a pale yellow substance which melted at 116° C. after recrystallising from alcohol. The yield (1 gram) was poor—as was to be expected (*cf.* Roberts and Turner, *J.C.S.* (1927), 1832-

1857). (Found, C = 66·9, H = 4·8%; calculated for $C_{19}H_{17}O_5N$, C = 67·2, H = 5·0%.)

2-Veratryl-7-methoxyquinoline-4-carboxylic acid (IV).

This acid was obtained almost at once (yield 3·5 g.) from a boiling alcoholic solution of m-anisidine (4 g.), veratric aldehyde (5 g.) and pyruvic acid (3 g.). After recrystallisation from alcohol the flaky yellow crystals melted at 222° C. (Found, C = 67·3, H = 5·4%; calculated for $C_{19}H_{17}O_5N$, C = 67·2, H = 5·0%.)

2-Veratryl-6-methoxyquinoline-4-carboxylic acid (V).

After refluxing a solution of p-anisidine (3·5 g.), veratric aldehyde (5 g.) and pyruvic acid (3 g.) in alcohol (100 cc.) for three hours, the product (2 grams) crystallised on cooling. Recrystallised from alcohol it was obtained in flaky yellow platelets melting at 257° C. (Found, C = 67·1, H = 5·5%; calculated for $C_{19}H_{17}O_5N$, C = 67·2, H = 5·0%.)

2-Veratryl-7-hydroxyquinoline-4-carboxylic acid (VI).

This substance was precipitated as a yellow powder (3·5 g.) after heating a solution of m-aminophenol (4 g.), veratric aldehyde (5 g.) and pyruvic acid (3 g.) in alcohol (150 cc.) for a few minutes. As it is insoluble in ordinary organic solvents it was purified by solution in concentrated potassium carbonate solution and treatment of this in the hot with animal charcoal, followed by filtration and acidification of the filtrate with acetic acid. After washing and drying the purified cinchoninic acid was found not to melt below 300°. (Found, C = 66·3, H = 4·9%; calculated for $C_{18}H_{15}O_5N$, C = 66·4, H = 4·6%.)

2-Veratryl-6-hydroxyquinoline-4-carboxylic acid (VII).

Refluxing p-aminophenol (3 g.), veratric aldehyde (5 g.) and pyruvic acid (3 g.) in alcohol (80 cc.) for a

few minutes led to the formation of this cinchoninic acid which was precipitated as a yellow powder (1·5 grams). As it also is insoluble in organic solvents it was purified in the same way as the previous substance. It did not melt below 300°. (Found, C = 66·0, H = 4·4%; calculated for $C_{18}H_{15}O_5N$, C = 66·4, H = 4·6%.)

2-Veratryl-7-dimethylaminoquinoline-4-carboxylic acid (VIII).

Refluxing m-dimethylamino-aniline (5 g.) veratric aldehyde (6 g.) and pyruvic acid (3·5 g.) in alcohol (80 cc.) for fifteen minutes led to ready condensation and the dimethylamino acid crystallised out. Recrystallised from glacial acetic acid it was obtained as a deep orange powder melting at 259°. (Found, C = 68·0, H = 6·1%; calculated for $C_{20}H_{20}O_4N_2$, C = 68·2, H = 5·7%.)

$\alpha:\alpha^1$-Diveratryl-phenanthroline-$\gamma:\gamma^1$-dicarboxylic acid (IX).

This substance was readily obtained by refluxing a solution of m-phenylene diamine (5 g.), veratric aldehyde (16 g.) and pyruvic acid (8 g.) in alcohol (150 cc.) for one hour. A dark oily substance separated and this readily solidified on cooling. Yield 15 grams. Recrystallised from alcohol it formed a light red powder melting at 191°. (Found, C = 66·6, H = 4·0%; calculated for $C_{30}H_{24}O_8N_2$, C = 66·7, H = 4·4%.)

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A NOTE ON THE CONSTITUTION OF "TASMANOL."

By V. M. TRIKOJUS, B.Sc., D.Phil.,

and D. E. WHITE, M.Sc.

(Read before the Royal Society of New South Wales, Sept. 7, 1932.)

Smith and Robinson (this Journal, 1914, **48**, 518) first reported the occurrence of phenolic substances in the leaf-oil of the Eucalypts. The two substances isolated were tentatively called "Tasmanol" and "Australol," the constitution of the latter having been subsequently shown to be that of p-isopropyl phenol (Earl and Trikojus, *ibid.*, 1926, **59**, 301).

"Tasmanol," which occurs in greatest quantity in the oils of the cineol-phellandrene bearing class, particularly *Eucalyptus linearis* and *E. Risdoni*, was described by Smith and Robinson as containing one methoxyl group and probably two phenolic groups in the para position, but they gave no analytical figures or other data from which these conclusions were drawn. Its most characteristic property is the blood-red colour which it gives with ferric chloride solution.

In order that the constitution of this substance might be more fully investigated, 50 kilograms of the leaves of *E. Risdoni* were obtained from Tasmania, submitted to steam distillation, and the oils so obtained extracted with alkali. The amount of alkali-soluble material obtained was disappointing, being only 0·012% (6 g.).

Until a further supply of raw material arrives, it was thought advisable to report the results so far obtained, as these indicate that the structure of "Tasmanol" differs fundamentally from that suggested by Smith and Robinson.

The material obtained during the present investigation was found to be mostly soluble (75%) in sodium carbonate solution (6%), and of this portion 55% distilled over a range of 3°, under diminished pressure. Re-distillation yielded what appeared to be a pure substance. It gave a pronounced red colour with alcoholic ferric chloride, was completely soluble in sodium carbonate solution, and in the other alkalis, liberated methyl iodide with hydriodic acid, decolorised bromine water, and appeared to be an acid, as the derivative, obtained by treating it with methyl alcohol and hydrochloric acid gas, was readily hydrolysed by aqueous potassium hydroxide (20%). Analyses showed it to have the constitution $C_{13}H_{22}O_3$, whilst a crystalline p-toluidide and a silver salt were obtained, but unfortunately in an insufficient quantity for analysis.

Examination of a small specimen of "Tasmanol," of unknown origin, prepared by the late H. G. Smith showed it to be completely soluble in sodium carbonate solution (Smith and Robinson, reporting "Tasmanol" as "partly soluble"), to decolorise bromine water, and that it could be esterified with methyl alcoholic hydrochloric acid, and the ester hydrolysed, although no crystalline p-toluidide or silver salt could be obtained.

Thus, although definite conclusions cannot be arrived at, at this stage, it seems that "Tasmanol" is an acid rather than the phenol suggested by Smith and Robinson. The red colour obtained with alcoholic ferric chloride would then be due to the formation of a coloured ferric

salt. A skeleton is suggested for the substance obtained in the present investigation in which a cyclohexene (or bridged cyclohexene) residue has attached to it a methyl ether grouping, and a carboxyl grouping (perhaps in an aliphatic side-chain), *viz.*, $C_6(C_5.H_{18})(O.CH_3)(COOH)$.

Experimental.

Alkali soluble oil obtained from 50 Kg. *E. Risdoni* leaves: 10 g. (containing a little benzene).

Soluble in sodium carbonate solution (6%):	4·5 g.
Red with $FeCl_3$	
Insoluble in sodium carbonate solution (6%):	1·5 g.
Crimson with $FeCl_3$	
	6·0 g.

Distillation of Soluble Fraction.

1.	B.p. 110-113° at 0·5 mm.	2·5 g.
2.	B.p. 115-125° at 0·5 mm.	1·0 g.
3.	Residue	1·0 g.

Fraction 1 Redistilled.

a.	B.p. 80-105° at 0·5 mm.	0·25 g.
b.	B.p. 107-9° at 0·5 mm.	2·25 g.

Analysis (Fraction 1, *b*).

0·0786 g. gave 0·1988 g. CO_2 and 0·0685 g. H_2O

0·0769 g. gave 0·1960 g. CO_2 and 0·0680 g. H_2O

C : 69·0, 69·4%

H : 9·69, 9·83%

Calculated for $C_{13}H_{22}O_3$: C : 69·00%

H : 9·71%

Demethylation.—"Tasmanol" (from *E. Risdoni*) (0·3 g.) was treated with hydriodic acid (constant boiling; 10 cc.), the mixture being refluxed for 3 hours.

Methyl iodide was evolved, as evidenced by the precipitation of silver iodide from alcoholic silver nitrate solution. Water was added to the residue which was then extracted with ether. On removing the ether, a small quantity of oil was obtained which gave a pronounced red colour with alcoholic ferric chloride.

Methylation.—"Tasmanol" (0·25 g.) was dissolved in methyl alcohol (10 cc.), saturated with hydrogen chloride, and refluxed for 1 hour. Water and ether were added, the ethereal extract being washed with 5% sodium carbonate solution. The ethereal extract on evaporation yielded an oil (0·2 g.) which gave no colour with ferric chloride and was insoluble in sodium hydroxide solution in the cold. "Tasmanol" recovered: 0·05 g.

Hydrolysis.—The methylation product (0·2 g.) was refluxed for 2 hours with 20% aqueous potassium hydroxide (10 cc.). The product was then washed with ether, acidified and extracted with ether. Yield: 0·2 g. It gave a red colour with ferric chloride.

p-Toluidide.—"Tasmanol" (0·1 g.) was treated with thionyl chloride (0·5 cc.), excess of the latter removed and the residue taken up in ether and treated with excess p-toluidine in ether. The ethereal solution was then washed with dilute hydrochloric acid and water and the ether removed. The crystalline product thus obtained was purified by recrystallisation from petroleum ether. Yield: 0·04 g. M.p. 88-9° (constant).

Silver Salt.—"Tasmanol" (0·1 g.) was dissolved in the minimum amount of ammonia (0·5%) and excess silver nitrate solution added. A copious white micro crystalline precipitate of the silver salt was obtained. Yield: 0·1 g. The salt may be recrystallised from water in which it is only sparingly soluble.

"Tasmanol."

(Prepared by the late H. G. Smith.)

The specimen was purified by distillation, B.p. 115-122° (1·4 mm.). It was completely soluble in sodium carbonate solution, and gave a pronounced red colour with ferric chloride.

p-Toluidide.—0·5 g., treated with thionyl chloride and then with p-toluidine in the usual way gave a product which was mainly oily, although it appeared to contain some crystalline material.

Silver Salt.—On treatment of a solution of the ammonium salt with silver nitrate solution, no precipitate of the silver salt could be obtained.

Methylation.—0·3 g., dissolved in methyl alcohol (10 cc.) was refluxed for 45 minutes with the addition of 2 drops of pure sulphuric acid. Water and ether were added and the ethereal extract washed with sodium carbonate solution. Yield: 0·2 g. No colour with ferric chloride. Unchanged acid: 0·1 g.

Hydrolysis.—The above methylation product (0·2 g.) was refluxed for 2 hours with 10 cc. of 20% aqueous potassium hydroxide. The solution was then washed with ether, acidified and extracted with ether. Yield: 0·2 g. Red colour with ferric chloride.

We desire to thank Mr. J. McLeod of the University of Tasmania for his generous co-operation in obtaining supplies of raw material.

One of us (D.E.W.) is indebted to the Senate of the University of Sydney for a Science Research Scholarship, which enabled him to take part in this investigation.

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THE CHEMISTRY OF THE CONSTITUENTS OF THE WOOD-OIL OF THE "CALLITRIS" PINES.

PART I.

THE CONSTITUTION OF "CALLITROL."

By V. M. TRIKOJUS, B.Sc., D.Phil.,
and D. E. WHITE, M.Sc.,

(*Read before the Royal Society of New South Wales, Sept. 7, 1932.*)

The *Callitris* is the typical native pine of Australia, its distribution, in fact, extending over the whole continent. In New South Wales the predominant species is *Callitris glauca,* which grows in the valleys and on the plains, while *C. calcarata* is restricted to the hilly areas. Seven other species also occur but are not nearly so widespread. Several more species occur in West Australia and Tasmania, while *C. intratropica* is the predominant type in Northern Australia.

Although systematic work, founded on the morphological characters, was undertaken by the early botanists, the genus was much more fully investigated by R. T. Baker and H. G. Smith, who in their work, "*A Research on the Pines of Australia*" (Sydney, 1910), published details of the histology, physiology, phylogeny, embryology and chemistry of the genus.

In the chemical section they investigated the oils obtained by steam distillation of the leaves and of the wood. In the leaf-oils they found pinene, dextro- and lævo-limonene, dextro-borneol and bornyl acetate,

geraniol and geranyl acetate. These were generally present, but varied in amount in the different species in such a manner that the species could be identified by the composition of the leaf-oil.

It has long been known that the wood of the cypress pine is one of the very few timbers which shows immunity to termite attack (*cf.* Baker and Smith, *loc. cit.*; Oshima, *Philippine Journ. Science*, 1919, **25**, 319). The wood examined by Baker and Smith, from a chemical view-point, was chiefly that of *C. glauca.* Steam distillation of the wood, cut into shavings, gave 0·82% of oil after 8 to 9 hours. From this, there were isolated the sesquiterpene alcohol guajol, a probable sesquiterpene and a phenol to which they gave the name "Callitrol." To the presence of the latter substance were ascribed the characteristic odour of the timber, and its property as a white-ant deterrent. Oshima, however, regarded the anti-termitic properties as due to the presence of guajol.

The whole question was re-opened by the Forest Products Division of the Council for Scientific Industrial Research, and it is in collaboration with them that the chemistry of the constituents was undertaken in these laboratories.

Preliminary experiments (*J. Council Sci. and Ind. Research*, **2**, 178), having indicated that the alkali soluble extract from the wood-oil, rather than the guajol, was the material responsible for the resistance of the timber to fungi (*e.g.*, *Fomes annosus*), and termite attack, it was therefore highly desirable that the constitution of this material should be investigated, with the added object of studying the types of substances which act as termite deterrents.

Shavings of logs of *C. glauca* used in the present investigation were steam-distilled, as described in the

experimental part, and the oil so obtained extracted with sodium hydroxide. The major part of the alkali-soluble portion distilled over a small range, and consisted apparently of a chemical individual—"Callitrol." Re-distillation gave a product *completely soluble* in aqueous solutions of sodium carbonate and bi-carbonate, and when submitted to the following tests, as suggested by Baker and Smith, gave negative results in each case:

1. With bromine in alcohol.	Purple colour on evaporating the alcohol.
2. With bromine in acetic acid.	Red colour changing to purple and indigo-blue. Destroyed by water.
3. With sulphuric acid in acetic acid.	Red colour changing to deep purple.
4. With sulphuric and nitric acids in acetic acid.	Colour changes from red to purple but more rapidly.

The crude alkali-soluble oil gave the characteristic test described by Baker and Smith: "A drop of the oil on a watch glass is dissolved in acetic acid, and bromine vapour passed over it. A purple colour forms, soon becoming a rich purple." This, however, was found to be due, not to the main constituent of the alkali-soluble oil, but to a substance contained in a small fraction (11%) of higher boiling point. It may also be noted that the characteristic odour of the cypress pine is not due to "Callitrol," which, in the pure state, is almost odourless. Toxicity tests carried out on the carefully purified "Callitrol" used in the present investigation showed it to be the active principle in the alkali-soluble portion of the wood-oil. "Callitrol" was found to be optically active ($[\alpha]_D^{24°} = -6{\cdot}60°$), and soluble in the usual alkalis, with the exception of ammonia, although a crystalline substance, which liberated ammonia on exposure to the air, was obtained by passing dry ammonia gas into the petroleum ether solution. It gave

a faint red colour with alcoholic ferric chloride solution, and decolorised bromine water. Treatment with dimethyl sulphate and sodium hydroxide gave a methyl derivative which, however, was readily hydrolysed on refluxing with potassium hydroxide solution, the original "Callitrol" being recovered.

This seemed to indicate that "Callitrol" was not a phenol, and this was supported by analyses for carbon and hydrogen in conjunction with molecular weight determinations made on the methyl derivative. These indicated the formula $C_{10}H_{18}O_2$ for "Callitrol," and $C_{11}H_{20}O_2$ for the methyl derivative. The molecular weight of the "Callitrol" could not be accepted, the high values obtained increasing with the concentration, thus indicating that the substance was associated in solution. On reduction in ethyl acetate solution, in the presence of platinum oxide, two atoms of hydrogen were added, a colourless oil "Dihydrocallitrol" being obtained in quantitative yield. This substance was fully saturated, thus indicating an open chain structure for "Callitrol." "Dihydrocallitrol," like "Callitrol," was soluble in alkalis, and yielded a methyl derivative, which could be readily hydrolysed.

From the above results it seemed practically certain that "Callitrol" was an open chain acid containing one double bond. Further confirmation was obtained by the preparation of a crystalline silver salt, and also an acid chloride, by the action of thionyl chloride, from which was obtained a crystalline anilide. The amide and p-toluidide were obtained in a similar manner, together with the amide and anilide of the dihydro derivative. "Dihydrocallitrol" also yielded an anhydride on treatment with acetyl chloride at 120–180°.

By comparison of the properties of these derivatives of "Dihydrocallitrol" with those of the known acids $C_{10}H_{20}O_2$ it appeared certain that it was identical with dihydro-citronellic acid, the amide and anilide having similar melting points to those described, while the refractive indices of the acids were also in agreement.

In the case of the unreduced, citronellic acid, the only derivative described in the literature is the amide, and, although its melting point agrees with that of the amide of "Callitrol," this was not considered sufficient identification; in fact, there is only a very meagre literature devoted to the decenoic acids. It was, therefore, desirable to obtain some citronellic acid for comparison, and as neither *l*-citronellal nor the lævo-acid was available, the dextro-acid was prepared from d-citronellal, as outlined in the experimental part. The acid obtained in this way was then converted into the acid chloride with thionyl chloride, and this on treatment with aniline and p-toluidine in ether gave the anilide and p-toluidide, respectively. These were found to have melting points identical with the corresponding derivatives of "Callitrol." Mixtures of the anilides, *etc.*, of the dextro and lævo acids, however, showed a depression of melting point, but this is quite normal when no true racemate is formed.

Finally, distillation of the calcium salt of "Callitrol" with calcium formate gave a small yield of an aldehyde, which on conversion into the corresponding "atophan" had a melting point identical with that obtained from d-citronellal.

Thus, the main constituent of the alkali-soluble fraction from the wood of the Callitris pines is not a phenol, but *l*-citronellic acid (*i.e.*, $(CH_3)_2C:CH.CH_2.CH_2.CHCH_3.CH_2.COOH$). This appears to be the first record

of the occurrence of the lævo-form in nature. Realising the significance of these results, the synthesis and examination of a series of decenoic acids have been carried out, and in addition the dihydrocitronelloyl residue has been introduced into a number of phenols in the hope of securing valuable physiologically active substances. The outcome of these experiments, together with those on the constitutional study of guajol, will be shortly submitted for publication.

It is interesting to observe that experiments kindly carried out by Mr. Dadswell of the Forests Products Division of the Council for Scientific and Industrial Research, on carefully purified specimens, showed that while *l*-citronellic acid is completely toxic to the wood-destroying fungus (*Fomes annosus*) at a concentration of 0·016%, the dextro acid is slightly less toxic, while *l*-dihydrocitronellic acid manifests a similar toxicity to the unreduced acid.

Experimental.

The wood, after removal of the bark, was cut into shavings, distilled with a rapid current of steam, and the condensed vapours submitted to an automatic four-fold extraction with benzene. The following are the results from a typical distillation (from 33·95 kg.):

First day (5 hours)	210 g.
Second day (6 hours)	95 g.
Third day (5 hours)	34 g.
	339 g.

The oil was not completely free from benzene.

Alkali Extraction.—This was carried out by shaking the oil for some hours in contact with aqueous sodium hydroxide (5%). Ether was then added and the two layers separated. The ethereal layer was then extracted

several times with sodium hydroxide solution (5%), the alkaline extracts combined, washed with a little ether, and then acidified, after which the alkali soluble oil was extracted with ether.

Alkali—		
Soluble	118 g.	54%
Insoluble	101 g.	46%
	219 g.	

This corresponds to a 0·63% yield of crude oil.

Fractionation.—The alkali soluble portion (118 g.) was distilled under reduced pressure and the following fractions collected:

1.	B.p. –121°, at 0·7 mm.:	6 g.	..	5%
2.	B.p. 118–120°, at 0·55 mm.:	82 g.	..	70%
3.	B.p. 120–135°, at 0·55 mm.:	5 g.	..	4%
4.	Residue.	20 g.	..	18%

Re-Distillation of Fraction (2).

2. (*a*)	B.p. –114° at 0·4 mm.:	2 g.
2. (*b*)	B.p. 116 –7° at 0·5 mm.:	27 g.
2. (*c*)	B.p. 116·5–8° at 0·5 mm.:	50 g.
	Residue.	8·5 g.

Action of Bromine Vapour.—The following results were obtained when the various fractions were submitted to the "characteristic" test for "Callitrol" described by Baker and Smith and mentioned previously:

Crude Oil (Positive)
- Alkali Soluble (Positive)
  - 1. Negative.
  - 2. Positive.
    - *a.* Negative.
    - *b.* Negative.
    - *c.* Negative.
    - Res. Positive.
  - 3. Strongly Positive.
  - Res. Negative.
- Alkali Insoluble (Negative)

This table shows conclusively that the substance responsible for this colour reaction is contained exclusively in the small fraction boiling at a higher temperature than the main bulk, and totalling only 11% of the alkali soluble oil. Even then it is certain that this fraction is by no means pure, so that the amount of the substance causing the colour must be very small.

Fraction 2 (*c*) was redistilled, when it was found to have the following properties: B.p., 117-9°, at 0·6 mm. Refractive index at 24° : 1·4563. S.G. (25°/25°), 0·9274. α (24°; in 5 cm. tube) : –2·81°, *i.e.*, $[\alpha]_D^{24°}$: –6·60°. The substance was completely soluble in sodium carbonate and bicarbonate and calcium hydroxide solutions. On passing dry ammonia gas into the petroleum ether solution a crystalline precipitate was obtained which liberated ammonia when removed from the solvent. (Found: C, 70·4, 69·9; H, 10·3, 10·2, $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6%).

Molecular Weight:

In 1·286%	benzene	solution	M.W. : 292·1
„ 1·924%	„	„	M.W. : 302·6
„ 2·390%	„	„	M.W. : 317·2

Calculated for $C_{10}H_{18}O_2$, 170. These results indicated that association had occurred.

Methylation of "Callitrol".—"Callitrol" (7 g.) was dissolved in aqueous sodium hydroxide (20%; 50 cc.), and treated with dimethyl sulphate (20 cc.). The resulting insoluble oil was extracted with ether, the extract washed with sodium hydroxide solution, and then with water, dried, the ether removed and the product distilled.

Yield: 6 g. B.p. 86°, at 1·1 mm. (Found: C, 71·5, 71·4; H, 10·5; 10·9. $C_{11}H_{20}O_2$ requires C, 71·7; H, 10·9%.)

Molecular Weight in Benzene:

In 0·827%	benzene	solution	M.W. = 181·7
„ 1·031%	„	„	M.W. = 182·2

$C_{11}H_{20}O_2$ requires 184.

Hydrolysis.—The methyl derivative was refluxed with aqueous potassium hydroxide (6 g. in water, 100 cc.) for one hour. The oil was then completely dissolved, and after cooling and washing with ether, the alkaline solution was acidified with dilute hydrochloric acid and extracted with ether. The ethereal extract was washed with water, dried, and after removal of the ether, distilled.

Yield: 3 g. B.p. 120–1°, at 0·8 mm. (This is in very good agreement with that of the original "Callitrol.")

Reaction with Bromine.—As "Callitrol" had been observed to be unsaturated it was titrated with bromine in chloroform in an attempt to ascertain the number of double bonds present in the molecule. The bromine solution (0·03932 g. bromine per cc.) was run into a solution of "Callitrol" in chloroform cooled to 0°, until the colour of the bromine just persisted.

The chloroform solution was then shaken with water and the hydrobromic acid solution so obtained titrated with standard sodium hydroxide solution.

1. 0·2290 g. "Callitrol" absorbed 7·5 cc. bromine solution, and gave 0·06537 g. hydrogen bromide.
2. 0·3537 g. "Callitrol" absorbed 11·3 cc. bromine solution, and gave 0·0998 g. hydrogen bromide.

Thus 1 molecule absorbed 2·7 atoms of bromine and 0·6 molecule of hydrogen bromide were liberated.

From this it appears that there is one double bond in the molecule, but one atom of hydrogen is also being substituted with bromine.

Reduction of "Callitrol."—"Dihydrocallitrol."

"Callitrol" was reduced, catalytically, in several solvents, with the following results:

1. *In Glacial Acetic Acid.*—"Callitrol" (5 g.) was dissolved in glacial acetic acid (50 cc.) and platinic oxide (0·35 g.) added. The mixture was then shaken with hydrogen, when the oxide was very quickly reduced, the absorption of hydrogen being complete in 2½ hours, when 835 cc. had been absorbed. The platinum was then removed by filtration and the acetic acid distilled from the water bath at 25 mm. The product was then distilled. Yield: 4 g. B.p. 113–5°, at 0·55 mm. Refractive index: 1·4365 (24°). Optical rotation: –2·0° (at 23·5° in a 5 cm. tube). "Dihydrocallitrol" was completely soluble in sodium carbonate and bicarbonate solutions.

2. *In Absolute Alcohol.*—"Callitrol" (25 g.) was dissolved in absolute ethyl alcohol (120 cc.) and platinic oxide (1 g.) added. The mixture was then shaken with hydrogen till absorption was complete. Hydrogen absorbed: 4030 cc., *i.e.*, one molecule. The platinum was then removed by filtration and the alcohol evaporated. The product was then distilled. Yield: 20 g. B.p. 114–6°, at 0·62 mm.

3. *In Ethyl Acetate.*—"Callitrol" (15 g.) was dissolved in ethyl acetate (75 cc.) and platinic oxide (1·0 g.) added. The mixture was then shaken in an atmosphere of hydrogen until absorption was complete (2560 cc. absorbed). The platinum was then removed by filtration and the ethyl acetate evaporated. The product was then distilled. Yield: 13·5 g. B.p. 114–5°, at 0·7 mm. Refractive index: 1·4370 (23°). Optical rotation: –1·91° (at 22° in a 5 cm. tube). This was the most satisfactory of the methods of reduction tried, the platinum coagulating easily when the reaction was complete and the solvent being easily removed on the water bath. (Found: C, 69·8, 70·3%; H, 11·4, 11·7. $C_{10}H_{20}O_2$ requires C, 69·8; H, 11·6%.)

Action of Methyl Alcohol and Hydrochloric Acid on "Callitrol."—"Callitrol" (5 g.) was dissolved in methyl alcohol (21 g.) and dry hydrochloric acid gas (1·5 g.) passed into the solution while cooling in ice. The solution was then refluxed for 30 minutes, when it had darkened somewhat. The methyl alcohol was then distilled and the product dissolved in ether and washed with sodium hydroxide solution (10%) and then with water. The extract was then dried and the ether evaporated and the product distilled. Yield: 3·7 g. B.p. 85–88° at 0·4 mm. The substance contained chlorine, and as indicated by the following analytical figures consisted largely of the hydrochloro derivative of the methyl ester. (Found: C, 62·2, 62·3; H, 9·5, 9·7; $C_{11}H_{21}O_2Cl$. requires C, 64·8; H, 9·9%.)

Silver Salt.—"Callitrol" (2 g.) was dissolved almost completely in sodium carbonate solution. Excess silver nitrate solution was then added and the precipitated silver salt filtered and washed free from silver nitrate. It was then recrystallised from boiling water, in which it was slightly soluble. Addition of a little silver nitrate solution was necessary for the complete separation of the salt in recrystallisation. Colourless prisms. Yield: 0·5 g. (from 2 litres of water.)

As the salt decomposed on exposure to the light it was dried, in a vacuum desiccator in the dark. 0·1443 g. gave 0·0561 g. silver; 0·1398 g. gave 0·0541 g. silver; *i.e.,* molecular weight : 277·5, 278·8; *i.e.,* equivalent weight of "Callitrol" : 170·6, 171·9. Calculated for $C_{10}H_{18}O_2$: 170.

Anilide.—"Callitrol" (1 g.) was treated with thionyl chloride (1·5 cc.) with warming on the water bath. The excess thionyl chloride was then removed on the water bath at 25 mm. and the residue treated with aniline 1·5 cc. in 10 cc. ether). Heat was evolved and the reaction

was completed by warming on the water bath. The ethereal solution of the product was then washed with dilute hydrochloric acid, and then with water, the extract dried and the ether removed on the water bath. The residue crystallised on cooling and was recrystallised from petroleum ether. Yield: 0·7 g. M.p. 76°. This substance crystallised in long colourless prisms (needles). It was soluble in acetone, ethyl acetate, benzene, chloroform, ether and methyl and ethyl alcohols. It could be recrystallised from petroleum ether and aqueous methyl alcohol. It was practically insoluble in water. (Found: N, 5·7, 5·7. $C_{16}H_{25}ON$ requires N, 5·7%.)

Amide.—The acid chloride from "Callitrol" (1 g.) was treated with ammonia (S.G., 0·880; 10 cc.) and the brownish coloured product filtered, washed with water, and crystallised from petroleum ether, when it was obtained in colourless leaflets, m.p. 84–5°. Yield: 0·2 g.

p-Toluidide.—This was obtained from the acid chloride (from "Callitrol," 1 g.), as in the case of the anilide. It crystallised from aqueous methyl alcohol in colourless prisms, m.p. 93–4°. Yield: 0·4 g. (Found: N, 5·3, 5·3; $C_{17}H_{25}ON$ requires N, 5·4%.)

Anilide of "Dihydrocallitrol."—"Dihydrocallitrol" (1 g.) was converted into the acid chloride (as for "Callitrol," above), and then treated with aniline in ether. The product crystallised from aqueous methyl alcohol in colourless needles, m.p. 90–1°. Yield: 0·4 g. (Found: N, 5·6, 5·6. $C_{16}H_{25}ON$ requires N, 5·7%.)

Amide.—This was obtained from the acid chloride of "Dihydrocallitrol" as in the corresponding case of "Callitrol." It crystallised from petroleum ether in colourless leaflets, m.p. 108–9°. (Found: N, 8·1, 8·1, $C_{10}H_{21}ON$ requires N, 8·2%.)

Anhydride.—"Dihydrocallitrol" (5 g.) was heated in a small flask with reflux condenser to 120°. Acetyl chloride (2·5 g.) was then dropped in slowly, the temperature being allowed to rise during 30 minutes to 180°. The product was then distilled. The fraction (b.p. 154–6° (0·9 mm.); 2·5 g.) was insoluble in aqueous sodium carbonate solution even on long standing. On warming on the water-bath with aniline it rapidly yielded the anilide, m.p. 91–2°, unaffected by admixture with the product obtained from the acid chloride.

Aldehyde from "Callitrol."—"Callitrol" (17 g.), quicklime (2·8 g.), and calcium formate (6·5 g.) were mixed with a little alcohol and the mixture evaporated on the water bath to dryness. The product was finely powdered, mixed with an equal weight of purified sand, and distilled from a copper retort. The distillate (8 g.) was dried and fractionated, the fraction (b.p. 103–8° (27 mm.); 1·0 g.), was taken up in ether, washed with sodium carbonate solution, and redistilled. Neither the semicarbazone nor the 2:4-dinitro phenylhydrazone could be obtained crystalline, but the atophan was obtained by the action of β-naphthylamine and pyruvic acid in alcohol. This melted at 249° after purification from ethyl alcohol. The atophan obtained similarly from d-citronellal melted at 249°.

d-Citronellic Acid.—(*cf.* Semmler, *Ber.*, 1891, **24**, 208; *Ber.*, 1893, **26**, 2255). It was found preferable to prepare the acid from d-citronellonitrile, than by oxidation of d-citronellal with ammoniacal silver oxide. Full experimental details are not available in the literature, and the following are therefore submitted: *d-Citronellal* (154 g.), was dissolved in ethyl alcohol (200 cc.) and a solution of hydroxylamine hydrochloride (70 g.) in water (100 cc.) added. This was then treated with sodium

hydroxide (40 g.) in water (100 cc.) with vigorous stirring and the whole warmed on the water bath for 30 minutes. Water (300 cc.) was then added, the oil extracted with ether, and fractionated. The fraction (b.p. 143–8° (22 mm.); 71 g.) consisted of the oxime, a large proportion of the unconverted citronellal being recovered.

Nitrile.—The oxime (70 g.) and acetic anhydride (140 g.) were refluxed in an oil bath at 160° for two hours, and the product distilled. The fraction (b.p. 115–20° (23 mm.); 44 g.) consisted of the nitrile. The nitrile (10 g.) was heated under reflux with ethyl alcoholic potassium hydroxide (15 g. in 50 cc.) for 15 hours, when the evolution of ammonia was complete. The product was treated with steam to remove alcohol, unchanged nitrile and amide, washed with ether, acidified, and extracted with ether, and distilled. The fraction (b.p. 118–118·5° (0·55 mm.); 6·5 g.), had the following properties: α_D (5 cm. tube); –2·80°; refractive index: 1·4561 (21·5°). These physical properties are in remarkably good agreement with those of "Callitrol."

d-Citronellanilide.—This was prepared in the usual way *via* the acid chloride. It separated from aqueous methyl alcohol or petroleum ether in colourless needles, m.p. 75–6°.

A mixture with an equal weight of the anilide of "Callitrol," crystallised together from aqueous methyl alcohol, melted at 51–2°. (Found: N, 5·6, 5·7. $C_{16}H_{23}ON$ requires N, 5·7%.)

d-Citronell-p-Toluidide.—Prepared in the usual way, this separated from aqueous methyl alcohol in colourless elongated prisms, m.p. 93–4°. (Found: N, 5·3, 5·4. $C_{17}H_{25}ON$ requires N, 5·4%.)

COMPARISON OF THE PROPERTIES OF "CALLITROL" AND d-CITRONELLIC ACID.

	B.p.	α(5 cm. tube).	R.I.	Amide (m.p.).	Anilide (m.p.).	p-Toluidide (m.p.).
d-Citronellic acid	118-118·5° (0·55 mm.)	−2·80	1·4561 (21·5°)	84-5°	75-6°	93-4°
"Callitrol"	117-9° (0·6 mm.)	−2·81 (24°)	1·4563 (24°)	84-5°	76°	93-4°
d-Dihydrocitronellic acid			1·4373*	108-9°	91°	
"Dihydrocallitrol"	113-5° (0·55 mm.)	−2·0°	1·4365 (24°)	108-9°	90-1°	

* Wallach (Ann., 1898, **296**, 126.)

We make grateful acknowledgment to the executive of the Forests Products Division of the Council for Scientific and Industrial Research, the Queensland Forestry Board, and the District Forester at Dubbo for the supply of raw material.

One of us (D.E.W.) is indebted to the Senate of the University of Sydney for a Science Research Scholarship which has enabled him to take part in this investigation.

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THE SYNTHESIS OF BASES ALLIED TO CONIINE.

PART 1.

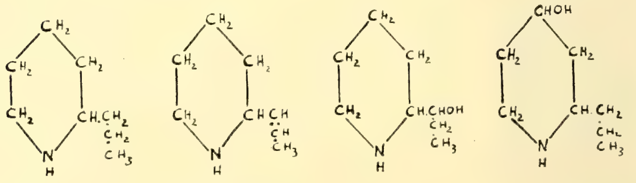
THE PREPARATION AND PYROLYSIS OF THE ALLYL ETHERS OF N-HETEROCYCLIC ENOLS.

By BURNETT MANDER-JONES, M.Sc.,

and V. M. TRIKOJUS, B.Sc., D.Phil.

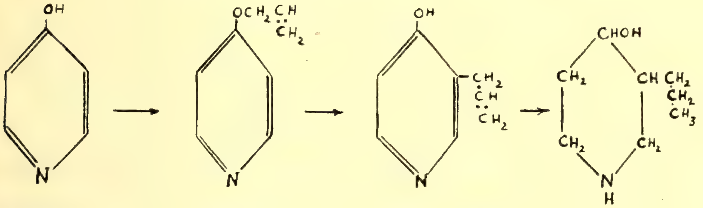
(Read before the Royal Society of New South Wales, Sept. 7, 1932.)

Coniine and its congeners (*e.g.*, I, II, III, IV), are among the simplest of the vegetable alkaloids, consisting essentially of a propyl-piperidine nucleus. The synthesis of d-coniine is one of the classics of synthetic organic chemistry. Although preparations containing these alkaloids have now disappeared from the British Pharmacopœia, it was considered interesting to associate the synthesis and physiological examination of allied substances, with a study of the Claisen "shift" of the allyl group in the case of the allyl-ethers of N-heterocyclic enols.



I. Coniine. II. β-Coniceïne. III. Conhydrine. IV. ψ-Conhydrine.

For example, formation of the allyl ether of 4-oxypyridine (V), might, on rearrangement, yield 3-allyl-4-oxypyridine (VI) which by reduction would lead conveniently to 3-propyl-4-piperidol (VII).

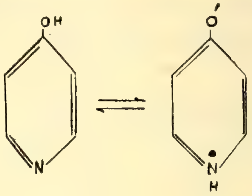


V. VI. VII.

In general, α-β unsaturated ethers of the type, R-O-C=C—, rearrange on heating, the group R passing to the β-carbon atom, particularly where R is the allyl group. This latter case has been extensively studied by Claisen and collaborators (*Ann.*, 1913, **401**, 21, *et seq.*), Hurd, and others (see Hurd, "The Pyrolysis of Carbon Compounds," *A.C.S.* Monograph, No. 50, 1929, Chapter 8). In the case of phenyl-allyl ethers, the allyl group migrates, on pyrolysis, to the ortho position and, if this be occupied, to the para position relative to the hydroxyl group. The inability of the saturated alkyl-aryl ethers to pyrolyse in this manner is attributed by Hurd (*loc. cit.*, p. 206) to the greater electropositivity of the allyl and related groups in which α-β unsaturation, relative to the ether linkage, is present.

α- and γ-Oxypyridines and quinolines show a marked tendency towards tautomerism to the oxo-form. Whether the pyridine-pyridone tautomeric change forms a true example of keto-enol tautomerism is debatable. According to Arndt and Kalischek (*Ber.*, 1930, **63**, 587, 2963) the relationship is best represented by the oxy-formula (VIII), and "Zwitterionic" formula (IX), O, and N

derivatives being analogously formulated. This betaine-formula (IX) appears to be the more stable configura-



VIII. IX.

tion, and numerous examples are recorded of the migration of the group R in N-heterocyclic enolic derivatives during pyrolysis. Thus Stolz, (D.R.P., 95693; C.1898, 1, 812) records the conversion of 1-phenyl-3-methyl-5-ethoxy pyrazole into the corresponding 2-ethyl pyrazolone; 4-methoxyquinoline yields N-methyl-4-quinolone between 300-310° (Meyer, M., 1906, **27**, 255); 4-methoxy quinaldine rearranges similarly (Conrad and Limpach, *Ber.*, 1887, **20**, 947); and 4-methoxy pyridine gives the analogous pyridone on heating above its boiling point (Haitinger and Lieben, *Ber.*, 1885, **18**, 929). Räth (*Ann.*, 1931, **484**, 452) records his inability to convert 2-methoxy-5-nitropyridine into N-methyl-5-nitro-2-pyridone. On the other hand, Tschitschibabin and Jeletsky (*Ber.*, 1924, **57**, 1161) claim to have pyrolysed 2-phenoxy pyridine and 2-phenoxy quinoline at dull red heat into the respective N-phenyl isomerides and to have detected the conversion of the 2-allyl into the N-ether on distillation. Hurd (*loc. cit.*, p. 205) remarks, in dealing with migrations in derivatives of N-heterocyclic enols, ". . . in these cases the alkyl group wanders to a nitrogen atom wherever it may be in preference to α-β unsaturated carbon." If the tautomeric nature of the oxy-pyridyl nucleus be concerned entirely with the mobility of a hydrogen atom between oxygen and nitrogen, and if a

quinone configuration be an invariable intermediate phase in the Claisen-rearrangement (*cf.* Fieser, *J.A.C.S.*, 1926, **48**, 3205; 1927, **49**, 857), it might be expected that in these cases also the allyl-group would migrate as in the case of other alkyl-groups.

From a study of the literature one could draw the following conclusions:

(*a*) The allyl group does not differ essentially from other groups in pyrolytic behaviour but only in degree.

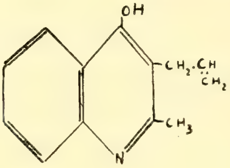
(*b*) Allylation of N-heterocyclic enols should give both N-and-O-allyl ethers analogously to methylation (*cf.* Friedländer and Müller, *Ber.*, 1887, **20**, 2009).

(*c*) O-Allyl ethers should pyrolyse to the N-ethers as is the case with other ethers.

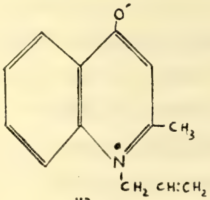
2-Alloxy-quinoline, the only substance of this type which has been prepared, was obtained from 2-chloro-quinoline and sodium allylate, but not definitely characterised (Tschtschibabin and Jeletsky, *loc. cit.*). The nature of the parent substances renders somewhat difficult the preparation of oxy-ethers by ordinary methods. The best procedure appears to be either by acting on the silver salt with the alkyl halide (*cf.* Räth, *loc. cit.*, Baltzer, *Ann.*, 1930, **480**, 172), or by the decomposition of the chloro-compound with a solution of the sodium alkoxide in the corresponding alcohol. During the present investigation the silver-salt method gave the best results.

The parent substances themselves are in many cases difficult to prepare, one of the simplest being 4-oxyquinaldine (Limpach, *Ber.*, 1931, **64**, 967). Allylation of this compound was readily achieved by decomposition of the silver salt with allyl bromide in methyl alcoholic suspension, and the extremely exothermic pyrolysis of the purified oil so obtained initiated by

simple heating at 180°. The crystalline rearranged product was obtained in theoretical yield. The decision between the two formulæ (X) and (XI) for this substance (neglecting the possibility of a migration into the "peri" position), was reached by a consideration of its properties and ultimately by its synthesis, using Knorr's method, from α-allyl-β-phenylaminocrotonic ester, which left no doubt as to the exclusion of (XI).

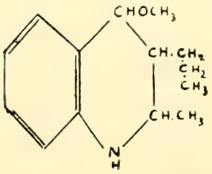


X.

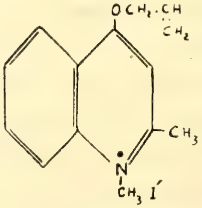


XI.

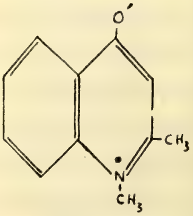
The substance (X) posesses only feeble enolic properties, giving a faint coloration with alcoholic ferric chloride, whilst the sodium salt is readily hydrolysed. However, it readily yielded an O-benzoyl derivative. Replacement of the hydroxyl group by chlorine using phosphorus pentachloride and oxychloride (*cf.* Conrad and Limpach, *loc. cit.*), followed by treatment with sodium methoxide yielded a methoxy derivative, and reduction of this substance to 2-methyl-3-propyl-4-methoxy tetrahydroquinoline (XII) was accomplished by Adams method. Three asymmetric carbon atoms are



XII.



XIII.

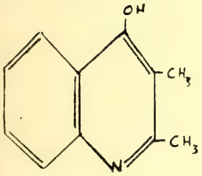


XIV.

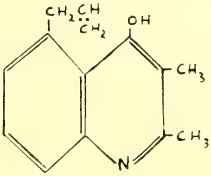
introduced by the reduction. The description and report on the physiological examination of this final product (which is being kindly undertaken by Dr. A. J. Canny), is reserved for a later communication.

It is interesting to observe that the methiodide (XIII) of the allyl-ether rearranged quantitatively on heating above its melting point to N-methyl-4-quinaldone (XIV) with the elimination of allyl iodide. Removal of the enolic ether grouping *via* the quarternary salt has been frequently recorded (*cf.* Conrad and Limpach, *loc. cit.*, Friedländer and Müller, *loc. cit.*). In this case, betaine formation takes place at a temperature just below that at which migration occurs in the case of the allyl-ether itself.

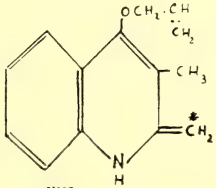
3-Methyl-4-hydroxy-quinaldine (XV) gave an additional anomalous result on allylation and pyrolysis (initiated at 190°). Even in this case the allyl group appeared to avoid nitrogen and to occupy a provisionally represented "peri" position (XVI).



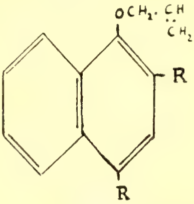
XV.



XVI.



XVI a.

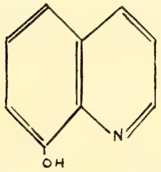


XVII.

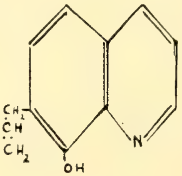
Although definite proof of the validity of structure (XVI) is not yet advanced, the temperature of formation and general properties of the substance point to the

exclusion of an N-allyl-quinaldone configuration. In the napthalene series pyrolysis of an allyl-ether of formula (XVII, R representing a blocking group) has not yet been studied. Possibly the group would likewise "shift" into the "peri"-position. An alternative consideration of the migration could assume the existence of a phase of the allyl ether involving $-N{=}C{-}CH_3 \rightleftarrows -NH{-}C{=}CH_2$. mobility (XVI*a*). The carbon atom ($\overset{*}{C}$) in the resulting conjugated system is analogous to a p-carbon atom, the allyl group possibly migrating to this position on pyrolysis with the formation, after redistribution of the affinities, of ω-allyl-3: methyl: 4-oxy quinaldine. This case would then be somewhat analogous to the pyrolysis of 2: 4-dimethyl-6-isoallyl-alloxybenzene (Claisen and Tietze, *Ann.*, 1926, **449**, 84).

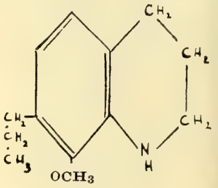
The proximity of oxygen and nitrogen in 8-oxy-quinoline (XVIII) lent some interest to the allylation of this substance, which was conveniently achieved by decomposition of the sodium or potassium salt with the allyl halide in methyl alcoholic solution. A strongly exothermic reaction occurred on heating the ether to 190°, yielding a homogeneous rearranged product containing phenolic hydroxyl.



XVIII.



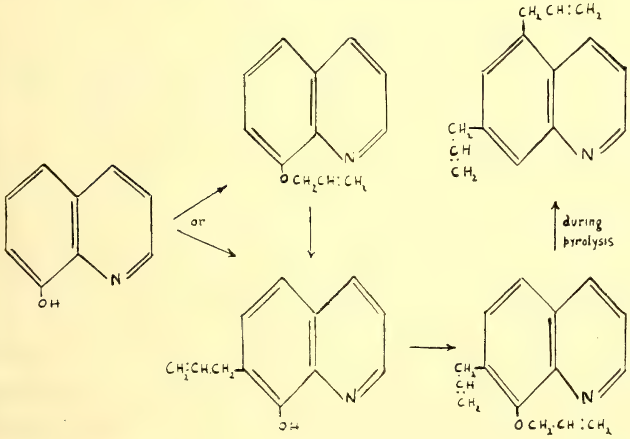
XIX.



XX.

Attempts to correlate this substance with 7-allyl-8-oxyquinoline (XIX) by synthesis of the latter from 2-allyl-6-aminophenol by Skraup's method were unsuc-

cessful. However, in view of the experience of Claisen, that the ortho-position, when vacant, is the one occupied, it seems reasonable to suppose an analogous migration in the present instance. Methylation was carried out with methyl sulphate and alkali and reduction with sodium and alcohol (*cf.* Emmert, *Ber.*, 1915, **48**, 688), yielded the piperidol derivative (XX), the physiological properties of which will be shortly reported. It is only mildly toxic. It is worthy of mention that in the preparation of the allyl-ether by distillation, the final runnings regularly solidified. This solid material (diallyl-8-oxyquinoline) apparently resulted from nuclear allylation (or possibly migration during the formation of the ether), plus oxyallylation, according to the following scheme, since the same substance was obtained by pyrolysis of the allyl-ether of 7-allyl-8-oxyquinoline. Its formula is provisionally represented as 5:7-diallyl-8-oxyquinoline (XXI). This initial nuclear allylation during the reaction, under such mild conditions, and particularly in a hydroxylic solvent, is unusual (*cf.* Claisen, *Z. angew. Chem.*, 1923, **36**, 478).



XXI.

So far, the results obtained do not permit of modified suggestions as to the mechanism of the Claisen rearrangement. A study on α-, β-, γ-oxypyridines themselves is almost concluded, and has provided interesting results. The work is being extended in other directions. Moreover, the study of the kinetics of the rearrangement has not yet received attention on a quantitative basis. Mr. L. W. O. Martin, B.Sc., of this University, has already begun exploratory experiments dealing with this aspect of the problem.

Experimental.

4-Oxyquinaldine.—In the preparation of this and allied substances by alcohol elimination from the corresponding β-arylamino-crotonic ester it was found that the esters gave improved products on pyrolysis if subjected to preliminary purification by distillation in high vacuum. The esters distil smoothly at 1-2 mm. pressure.

β-phenylamino crotonic ester (b.p. 145°, at 1·8 mm.) was cyclised in paraffin solution (*cf.* Limpach, *loc. cit.*) and the product recrystallised preferably from ether-alcohol.

4-Alloxyquinaldine.—The silver salt (57 g., precipitated from the sodium salt in aqueous-alcohol) of 4-oxyquinaldine, dried, and sieved, was suspended in an absolute ethyl alcoholic solution of allyl bromide (19 cc. in 100 cc.) and refluxed during four hours. After filtration from silver bromide (40·5 g.), concentration, and addition of sodium hydroxide solution (20%), the oil so obtained (32 g.) was extracted with ether and distilled at 1·2 mm. Yield, 15 g., b.p. 152-3°. Formation of a residue (12·5 g., in this instance), which consisted almost entirely of 3-allyl-4-oxyquinaldine (see below),

is difficult to prevent unless the temperature of the oil bath and the pressure be maintained at the lowest possible values. 4-alloxyquinaldine is a colourless oil, soluble in mineral acids and organic solvents. (Found: C, 77·8; H, 6·50; $C_{13}H_{13}ON$ requires C, 78·4; H, 6·53%). *Picrate* (yellow needles from methyl alcohol, m.p. 188°). *Methiodide* (colourless prisms from methyl alcohol; m.p. 165° (decomp.). Found: I, 37·3; $C_{14}H_{16}ONI$ requires I, 37·3%). *Hydrochloride* (colourless needles from alcohol-ether, m.p. 171-172°).

3-Allyl-4-oxyquinaldine (X).—4-alloxy quinaldine (5 g.) was heated to 180°. The internal temperature then rapidly rose to 270°, the rearrangement being being complete in 1 minute. (For the pyrolysis of larger quantities, dilution with a neutral solvent is advisable.) Solution in dilute hydrochloric acid and precipitation with ammonia yielded the colourless base (4·7 g., m.p. 270°). Crystallisation from methyl alcohol gave elongated prisms, m.p. 273°. (Found: C, 78·0; H, 6·5; $C_{13}H_{13}NO$ requires C, 78·4; H, 6·5%). 3-Allyl-4-oxyquinaldine is sparingly soluble in water, soluble in mineral acids, but insoluble in acetic acid. It gives a light red colour with alcoholic ferric chloride, but none in aqueous solution. A solution of the sodium salt may be obtained in aqueous-alcohol but hydrolysis readily occurs on addition of water. The silver salt (grey micro-crystalline powder) may be precipitated from the aqueous-alcoholic solution of the sodium salt. *Benzoyl derivative* (benzoyl chloride and alkali on the base; colourless prisms from aqueous methyl alcohol, m.p. 87-88°. Found: C, 78·9; H, 5·9. $C_{20}H_{17}O_2N$ requires C, 79·2; H, 5·6%).

α-Allyl-β-phenylamino crotonic ester.—*β*-Phenylamino crotonic ester (50 g.) in dry benzene (300 cc.) was

treated with sodium wire (5·7 g.). The resulting solution of the sodium salt was then decomposed by allyl iodide (46 g.). Heat was developed and after standing for some hours the reaction was completed by refluxing for one hour. Water was then added, and the benzene solution dried, evaporated, and distilled. The main fraction (34 g.) distilled at 161-162° (2 mm.). (Found: C, 73·0; H, 8·0. $C_{15}H_{19}O_2N$ requires C, 73·4; H, 7·8%.) Elimination of alcohol was accomplished by slowly raising the temperature of the crotonic ester from 225° to 260°. For quantities greater than 10 g. the paraffin oil modification of Limpach (*loc. cit.*) is desirable. After purification from methyl alcohol the product (3-allyl-4-oxyquinaldine) melted alone, or mixed with the rearranged product from 4-alloxy quinaldine, at 273°.

Decomposition of the Methiodide (XIII) of 4-alloxyquinaldine.—The methiodide (4 g.) was heated at a bath temperature of 175° during 17 minutes. A slight exothermic reaction occurred (resulting in a maximum rise in the internal temperature of 7°), and allyl iodide (1·0 g.) distilled. The dark coloured residue still contained iodine and was completely soluble in water, but difficult to purify, probably owing to the occurrence of secondary reactions with the allyl iodide. The decomposition was best effected at a low pressure (3 mm.), when the residue consisted of a mass of almost colourless needles, which, after one crystallisation from benzene, melted at 160° (mercuric chloride derivative, m.p. 186°; needles from water). Conrad and Limpach (*Ber.*, 1887, **20**, 947) have recorded 160° and 187° respectively for N-methyl-4-quinaldone (XIV) and its corresponding derivative.

4-Methoxy-3-allylquinaldine.—Methylation experiments with (*a*) sodium methoxide and methyl iodide in methyl

alcohol, (*b*) diazo-methane in ether-alcohol, or (*c*) methyl iodide and the silver salt, were unsuccessful. A good yield was obtained, however, *via* 4-chloro-3-allyl quinaldine. 3-Allyl-4-oxyquinaldine (11 g.), phosphorus pentachloride (12 g.) and phosphorus oxychloride (0·5 cc.) were mixed and heated at 130-140°, until the evolution of hydrogen chloride was complete (15 minutes). Ice was added, and the product then warmed, filtered, made alkaline with sodium hydroxide solution, extracted with ether and distilled. Yield: 7·5 g., b.p. 154° (3 mm.). A small quantity (3%) of a solid base (colourless prisms from aqueous alcohol, m.p. 182°) contaminated the product towards the end of the distillation. It was removed by solution of the chloro compound in petroleum ether and filtration. It was not further investigated. The chloro compound was quantitatively converted into the methoxy derivative by heating it for two hours at 130-140° in methyl-alcoholic sodium methoxide (sodium, 0·85 g., in methyl alcohol, 40 cc.). Colourless oil, yield: 6·5 g., b.p. 147-149° at 1·6 mm. *Picrate* (yellow silky needles from methyl alcohol, m.p. 143°. Found: C, 54·1; H, 4·4. $C_{20}H_{18}O_8N_4$ requires C, 54·3; H, 4·1%). Reduction of the methoxy compound to the methoxy tetrahydro-quinoline derivative (XII) was effected by (*a*) sodium and ethyl alcohol, or (*b*) platinum oxide-platinum black. The properties of the reduction product will shortly be reported.

3-Methyl-4-oxyquinaldine (XV).—a-Methyl-β-phenylamino-crotonic ester (b.p. 150-151°, 2 mm.) was prepared analogously to the allyl compound (*vide supra*, and *cf.* Conrad and Limpach, *Ber.*, 1891, **24**, 2990) and pyrolysed in paraffin oil at 240-250°.

3-Methyl-4-alloxyquinaldine.—3-Methyl-4-oxyquinaldine (6·5 g., m.p. 315°) was converted, *via* the sodium salt in

aqueous alcohol, into the silver salt, and the latter, dried and sieved, heated for three hours in methyl alcoholic (20 cc.) suspension with allyl iodide (6 g.). The procedure followed was then similar to that used in the case of the preparation of 4-alloxy quinaldine, with the exception that the allyl ether was purified through the picrate (5 g.), which crystallised from ethyl alcohol in balls of yellow needles, m.p. 161°. (Found: C, 54·2; H, 4·2. $C_{20}H_{18}O_8N_4$ requires C, 54·3; H, 4·0%.)

3-Methyl-4-oxy-5(?)-allylquinaldine.—The picrate (4 g.) of 3-methyl-4-alloxyquinaldine was decomposed with alkali and the oil obtained heated to 185° when the internal temperature rose to 205° and the product solidified almost immediately. It crystallised from methyl alcohol in colourless flat prisms, m.p. 249-250°. (Found: C, 78·4; H, 7·1. $C_{14}H_{15}ON$ requires C, 78·8; H, 7·0%). It was soluble in sodium hydroxide but the sodium salt was hydrolysed in dilute solution, insoluble in aqueous ammonia and soluble in mineral acids. It gave a pronounced red coloration with alcoholic ferric chloride.

8-Alloxyquinoline.—8-Oxyquinoline (60 g.) was dissolved in methyl alcohol (250 cc.) to which had been added potassium (16·2 g.), allyl bromide (50 g.) then added and the whole refluxed for six hours in an atmosphere of hydrogen. After removal of the alcohol, dilute sodium hydroxide was added, and the allyl ether extracted with ether and distilled. Yield: 55 g. (72%). A smaller yield (41%) was obtained by substituting sodium for potassium. 8-Alloxyquinoline is a colourless oil, b.p. 143-144° at 0·6 mm., non-volatile in steam, soluble in mineral acids and organic solvents. (Found: C, 77·4; H, 6·1. $C_{12}H_{11}ON$ requires C, 77·8; H, 6·0%). *Picrate* (yellow prisms from methyl alcohol, m.p. 148-

149°. Found: C, 53·6; H, 3·6. $C_{18}H_{14}O_8N_4$ requires C, 53·6; H, 3·4%). A small quantity of crystalline material (soluble in alkali, m.p. 83°) was obtained at the end of the distillation (see below).

7-Allyl-8-oxyquinoline (XIX).—8-Alloxyquinoline (53 g.) was rapidly heated (5 minutes) to 190° (external temperature). An internal thermometer registered 194° and in $1\frac{1}{2}$ minutes this had risen to 290°. The product was then distilled. The main fraction (47 g.; 89%), b.p. 139-142° (2 mm.), solidified, and melted constantly at 46° after one crystallisation from a concentrated solution in methyl alcohol. It crystallises in colourless needles, and is soluble in organic solvents, mineral acids, and dilute sodium hydroxide. The sodium salt may be crystallised from water but is more soluble in alcohol. (Found: C, 77·4; H, 5·9. $C_{12}H_{11}ON$ requires C, 77·8; H, 6·0%.) *Picrate* (yellow needles from alcohol, m.p. 190°). As in the distillation of the allyl ether, the final runnings yielded the base, m.p. 83° (2·5 g.).

5:7 (?)-Diallyl-8-oxyquinoline.—7-Allyl-8-oxyquinoline (2·7 g.) allyl bromide (1·8 g.) were refluxed for 5 hours in a methyl alcoholic solution of potassium methoxide (potassium, 0·6 g., in methyl alcohol, 12 cc.). The product was washed with alkali, extracted and distilled (2 g., b.p. 140°, 3 mm. *Picrate,* m.p. 135°). It was then pyrolysed at 190-240° (external temperature) during 5 minutes, and distilled at 2 mm. The distillate (1 g.) solidified and melted at 83° alone or mixed with the substance obtained above. (Colourless leaflets from methyl alcohol. Found: C, 79·6; H, 6·9. $C_{15}H_{15}ON$ requires C, 79·9; H, 6·7%). It dissolves in aqueous sodium hydroxide to a lyophyllic solution.

8-Methoxy-7-allylquinoline.—7-Allyl-8-oxyquinoline (20 g.) in sodium hydroxide (10%, 55 cc.) and methyl

alcohol (15 cc.) was shaken with dimethyl sulphate (13 cc.) during 30 minutes and finally heated for a similar period at 100°. The product was extracted with ether, washed with alkali and distilled. Yield: 14 g., b.p. 176-177° (16 mm.). It is a colourless oil, insoluble in water, soluble in acids. *Picrate* (yellow needles from methyl alcohol, m.p. 148-149°. Found: C, 53·2; H, 3·7. $C_{19}H_{16}O_8N_4$ requires C, 53·3; H, 3·7%).

8-Methoxy-7-isoallylquinoline.—The allyl compound (1·5 g.) was heated at 100° for 6 hours with ethyl alcoholic sodium ethoxide (sodium, 1 g., in alcohol, 15 cc.). Dilution with water and extraction with ether yielded an oil which was separated in quantitative yield as the picrate, m.p. 200° (yellow needles from alcohol. Found: C, 53·2; H, 3·8. $C_{19}H_{16}O_8N_4$ requires C, 53·3; H, 3·7%). (Note: During the present investigation it was found that analyses were preferably made on the picrates rather than on the parent bases, with which it was often difficult to obtain consistent results.)

The reduction product, 7-propyl-8-methoxy-tetrahydroquinoline will be described in a later communication.

Department of Organic Chemistry,
University of Sydney.

THE USE OF POTASSIUM DICHROMATE AND SODIUM NITRITE IN AROMATIC NITROSATIONS.

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D. P. Mellor, M.Sc.,
and V. M. Trikojus, B.Sc., D.Phil.

(With four text-figures.)

(Read before the Royal Society of New South Wales, Sept. 7, 1932.)

When a dilute solution of potassium dichromate and sodium nitrite is slowly distilled, nitrous acid passes over and may be collected to the extent of 91% (Marle, J., *J. Chem. Soc.*, 1909, **95**, 1493).

During the present investigation it has been found that this mixture may be utilised in organic chemical reactions as an excellent potential source of nitrous acid under neutral, or slightly alkaline conditions.

In solution, potassium dichromate gives an acid reaction owing to the hydrolysis of the dichromate ion, Cr_2O_7'', according to the following scheme, the final state being dependent upon the degree of dilution; the $HCrO_4'$ ion being thus common to dilute solutions of potassium dichromate, potassium chromate, and chromic acid (*cf.* Ephraim (Thorne), *Inorganic Chemistry*, Gurney and Jackson, London, 1926, pp. 386-7).

$$K_2Cr_2O_7 \rightarrow 2\dot{K} + Cr_2O_7'' \xrightarrow{H_2O} 2HCrO_4' \rightarrow 2\dot{H} + 2CrO_4''$$

or

$$K_2Cr_2O_7 + H_2O \rightarrow 2KHCrO_4$$

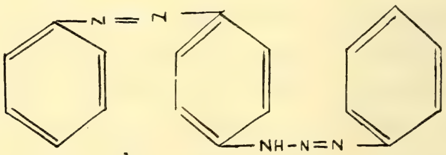
The modified equilibrated state, resulting from the introduction of two molecules of sodium nitrite, could then be disturbed by addition of heat, or of some substance (R.H.) which, under the attained conditions of hydrogen-ion concentration, would act as an acceptor of nitrite ions. Thus:

$$2\dot{K}+2HCrO_4'+2\dot{Na}+2NO_2'+2R.H.\rightarrow$$
$$2CrO_4''+2\dot{Na}+2R.NO+2H_2O$$

i.e.,

$$K_2Cr_2O_7+2NaNO_2+2R.H.\xrightarrow{H_2O}$$
$$2R.NO+K_2CrO_4+Na_2CrO_4+H_2O$$

If R.H. be aniline it has been found that conditions are propitious for the rapid production of pure diazoaminobenzene. Here it is highly desirable that the acidity of the solution be under careful control in order to counteract the formation of benzene-diazoamino-azobenzene, (1), the presence of which is said to account for the red colour obtained by treating ordinary specimens of diazoaminobenzene with alcoholic potassium hydroxide, and for the low melting points frequently recorded for this substance (*cf.* Earl, this Journal, 1930, **64**, 96).



1.

Thus, in Earl's preparative method (this Journal, 1929, **63**, 94, *cf.* Meunier, *Compt. rend.*, 1903, **137**, 1264) aniline, sodium nitrite, and carbon dioxide are utilised, the reaction, however, requiring 72 hours for completion, the product still giving a slight red colour with alcoholic

potassium hydroxide. From this, it would seem evident that diminution of the acidity of the solution, whilst reducing the possibility of the formation of (1) also diminishes the rate of reaction. Under the conditions outlined in the experimental part of the present investigation, it has been possible to carry out the reaction at practically a fixed pH value, the solution being throughout almost neutral, or slightly alkaline. When potassium dichromate, sodium nitrite, and aniline are used a very pure diazoaminobenzene is obtained after twenty minutes, with an initial pH of 4·85 (0·1 M. solution). The reaction was therefore carefully followed for changes in pH by means of the glass electrode. It was found that a rapid rise in pH took place, so that for nine-tenths of the reaction, the pH lay between 6·35 and 7·41. This initial increase, which rapidly brought about a buffered condition of the solution, was attributed to the formation of chromate ions during the reaction, thereby upsetting the following equilibrium:

$$K = \frac{[\dot{H}][CrO_4'']}{[HCrO_4']}$$

This was shown to be correct by the fact that one could reproduce the pH value, at any particular stage by the addition of the appropriate quantity of potassium chromate. A similar result was achieved by the addition of sodium or potassium hydroxides which provided the neutral chromate in solution. According to Britton (*J.*, 1924, **125**, 1572) sodium hydrogen chromate has, in dilute solution, an approximate pH of 4·5, and on titration with sodium hydroxide solution the curve obtained—using the hydrogen electrode—corresponds to that of the neutralisation of a weak mono-basic acid. We have found that, using the glass electrode, a

pH of 4·36 (0·1 M solution) is attained by potassium dichromate, the potassium hydroxide titration curve then following very closely that obtained for sodium hydrogen chromate. Thus, in solution, potassium dichromate may be considered as equivalent to potassium hydrogen chromate.

In a later extension of these observations, it was considered that since the following equation—

$$K_2Cr_2O_7 + XCO_3 \overset{H_2O}{\rightleftharpoons} K_2CrO_4 + XCrO_4 + CO_2$$

representing the reaction between carbonates and a solution of potassium dichromate, depends upon the application of heat for completion to the right (*cf.* Marle, *loc. cit.*), it would be of interest to utilise the reverse reaction, with the addition of sodium nitrite, for the preparation of diazoaminobenzene. Upon submitting an aqueous-alcoholic solution of aniline, sodium nitrite, and a small quantity of potassium chromate, to a current of carbon dioxide for 25 minutes, a quantitative conversion of the aniline to a diazoaminobenzene of high purity was obtained. In the absence of potassium chromate, diazoaminobenzene began to form only after a long period, (*cf.* Earl, *loc. cit.*). Apparently the small amount of potassium hydrogen chromate (potassium dichromate), produced by the reaction between the neutral chromate and carbon dioxide is sufficient to accelerate the reaction to a very marked degree. (Potassium dichromate has been prepared from potassium chromate and carbon dioxide under pressure; Goldstein (*J. Russ. Chem. Ind.*, 1926, 564), and Pincass (*Continental Met. Chem. Eng.*, 1927, **2**, 233). A similar result was, of course, achieved by substituting potassium dichromate for the chromate. This modification of the carbon dioxide method is suggested as the most con-

venient laboratory procedure for obtaining pure diazoaminobenzene.

By following the reaction between aniline, potassium dichromate, and sodium nitrite, electrometrically, with and without the addition of (*a*) potassium chromate, and (*b*) sodium hydroxide, it may be concluded that in such reactions, rapidity of acceptance of nitrous acid (or nitrite ion) does not entirely depend upon the acidity of the solution, since a rapid reaction can occur, within narrow limits, entirely on the alkaline side (*vide*, particularly, Fig. 2 and Fig. 3). No reaction occurred when disodium hydrogen phosphate was substituted for potassium dichromate, owing to the greater alkalinity of the solution (*vide* Britton, *J.*, 1927, 614).

The original mixture of dichromate and nitrite was successfully used for the preparation of a number of other diazoamino compounds, nitroso-methylaniline, and nitroso-thymol. Oxy-azo bodies (*e.g.*, 1-phenylazo-2-naphthol) were rapidly and quantitatively produced by this method, or by the carbon dioxide modification. Phenylene diamines, however, underwent oxidation, whilst diphenylamine was recovered unchanged. It is hoped to continue the investigation in these and other cases.

Experimental.

Preparative:

Carefully purified chemicals were used throughout.

Diazoaminobenzene (*a*).—Aniline (18·6 g.), and sodium nitrite (7·0 g.) in water (150 cc.) and methyl alcohol (100 cc.) were vigorously stirred, and cooled to below 5°. Potassium dichromate (14·7 g.) in water (200 cc.) was then added during 10 minutes, and the stirring continued for a further 10–15 minutes when the

conversion to diazoaminobenzene was complete. Recrystallisation from alkaline ethyl alcohol yielded pale yellow needles, m.p. 99·5°, which gave a light red colour with alcoholic alkali. Yield: 18·5 g.

Under similar conditions, 2:2′ and 4:4′ dimethyl diazoaminobenzene (m.ps., 59° and 119° respectively), were obtained from the corresponding toluidines. In the case of m-toluidine, the reaction was extremely slow, and only a viscous mass was isolated.

Nitroso-methylaniline (b.p. 124° (15 mm.). Yield—90%) was similarly prepared.

(*b*).—Potassium dichromate (14·7 g.) was mixed with potassium chromate (27·4 g.) and sodium nitrite (7·0 g.) in water (250 cc.), the whole being cooled in ice. Such a solution has an approximate pH of 7·0 (see Electrometric section, Table III). Aniline (18·7 g.) in methyl alcohol (50 cc.) was then added during seven minutes, with vigorous stirring, the temperature being maintained below 5°. Stirring was continued for a further 15 minutes, and the yellow crystalline powder filtered and washed with water and a little alcohol. The yield was quantitative, and the crude product gave only a faint red colour with alcoholic potassium hydroxide. After crystallisation from ethyl alcohol, it melted at 100·5° and gave practically no coloration with alcoholic alkali.

(*c*).—Aniline (18·6 g.), sodium nitrite (7·0 g.) and potassium chromate (1 g.) in water (100 cc.) and ethyl alcohol (80 cc.) were cooled in ice, and a current of carbon dioxide passed for 15–20 minutes. The yellow crystalline crude product gave only a light colour with alcoholic alkali.

1-Phenylazo-2-Naphthol: (*a*).—Aniline (9·3 g.) and β-naphthol (14·4 g.) in ethyl alcohol (80 cc.) was added

during 15 minutes to a well-cooled and stirred solution of potassium dichromate (14·7 g.), potassium chromate (10 g.) and sodium nitrite (7·0 g.) in water (300 cc.), the temperature remaining below 4°. Stirring was continued for a further 30 minutes. The crude product (22·8 g.) had m.p. 132° and 134° after recrystallisation from ethyl alcohol.

(*b*).—The above quantities of aniline, β-naphthol, and sodium nitrite in alcohol (150 cc.) and water (200 cc.) with the addition of potassium chromate (or dichromate; 1 g.) were cooled and treated with a rapid current of carbon dioxide for 30 minutes, when the conversion was complete. The crude product melted at 133°.

Nitroso-Thymol.—Thymol (15 g.) in ethyl alcohol (300 cc.) was added to potassium dichromate (14·7 g.), potassium chromate (15 g.) and sodium nitrite (7·0 g.) in water (250 cc.), and the whole maintained at 0° for a week, when the flask was filled with almost colourless crystals of nitroso-thymol (needles from benzene, m.p. 165-7°). In this preparation the reaction proceeds much more rapidly at the ordinary temperature; at 20° it was complete in 24 hours.

The Glass Electrode.

Haber's Glass Electrode was chosen in preference to the hydrogen electrode since it was necessary to carry out hydrogen ion measurements in solutions of potassium dichromate (*cf.* Hughes, *J.*, 1928, 501, for use of glass electrode with potassium dichromate—potassium chromate). The composition of the glass membrane used was that recommended by MacInnes and Dole (*J.A.C.S.,* 1930, **52**, 36). The glass was kindly supplied

by Mr. W. J. Lawrence of the Department of Physiology of this University. Small pieces of glass were fused on the end of a piece of $\frac{3}{8}''$ soda glass previously drawn out to a bore of $\frac{1}{10}''$. Bulbs of an approximate thickness of 0·025 mm. were then blown and allowed to stand for twenty-four hours in contact with decinormal hydrochloric acid. The cell was completed by a saturated calomel electrode and a silver/silver chloride electrode set up in the following manner:

Hg	Saturated KCl Hg_2Cl_2	Solution pH_x	Glass Electrode	$\frac{N}{10}$-HCl AgCl	Ag

The silver electrode was specially prepared (MacInnes and Beattie, *J.A.C.S.*, 1920, **42**, 1117). A Dolezalek quadrant electrometer with a fine phosphor bronze suspension was used as a null point indicator. To eliminate all possibility of short circuits, the needle was kept constantly charged by a 90 volt battery through a distilled water resistance. The leads to the electrometer were enclosed in earthed copper shields provided with paraffin plugs. The glass electrode, switches, *et cetera* were all placed in an earth zinc box and the whole apparatus placed on 2″ paraffin blocks (*cf.* Brown, *J. Sc. Inst.* 1924, 2, 12). A Cambridge Direct Reading potentiometer was used.

The cell was first standardised with a M/20 potassium hydrogen phthalate solution and then checked with other standard buffers. Each day before making measurements on the potassium dichromate mixture the electrode was standardised with M/20 potassium hydrogen phthalate pH 3·97. The following figures are given for

comparison of the apparatus with the hydrogen electrode:

Potassium hydrogen phthalate (M/20, pH, 3·97 (hydrogen electrode). E.M.F., 0·187 V.

Boric Acid (M/5; 18·8 cc.)–Borax (M/50; 1·2 cc.), pH, 7·09. E.M.F., 0·372 V. pH found, 7·15.

Boric Acid (M/5; 14 cc.)–Borax (M/20; 6 cc.), pH, 8·08. E.M.F., 0·432 V. pH found, 8·20.

Succinic Acid (M/20; 7·36 cc.), pH, 5·00. E.M.F., 0·250 V. pH found, 5·05.

Several determinations were made in the case of each buffer solution, the values given being averages with a maximum error of approximately ± 0·6%. Whilst following the course of a reaction the accuracy attained was probably not quite of the same order as here indicated for a reason explained below.

During the standardisation, neither the standardising buffer nor the solutions used for checking the electrode were left in contact with it for periods of longer than five minutes. However, if an electrode were left in contact with the standardising buffer overnight it was found that on replacing the buffer by a solution of different ionic composition the E.M.F. of the cell was steady for about five minutes. Thereafter it was subject to a small "drift," rose to a maximum in twenty minutes and then after two hours returned to the original value. Thus an electrode which had been left in contact with boric acid/borax buffer, pH 7·09, overnight was checked periodically with M/20 potassium hydrogen phthalate over ninety minutes. The following readings were obtained:

TABLE I.

Time. (Mins.)	E.M.F. (V.)	pH.
0	0·188	3·97
11	0·195	4·09
20	0·198	4·16
25	0·193	4·06
35	0·194	4·07
46	0·192	4·04
57	0·192	4·04
68	0·191	4·02
79	0·188	3·97
90	0·187	3·95
101	0·186	3·94
1000	0·190	4·00

In another experiment the following results were obtained: Two solutions of potassium dichromate and potassium dichromate–potassium chromate of pH 4·20 and 7·00 respectively were tested against a glass electrode which had stood in contact with M/20 potassium hydrogen phthalate overnight. For the solution pH 7·00 the E.M.F. gradually rose, and after several hours returned to a value corresponding to a pH of 7·01. The solution of pH 7·00 was then replaced by a dichromate solution of pH 4·20. The E.M.F. of the cell was then quite steady over twenty minutes. On restoring the phthalate buffer to the cell the E.M.F. agreed with that originally found with this buffer but again a small "drift" was noted. This effect was not so marked with electrodes which had been in use for some time. It was further minimised by allowing the glass electrode to stand in contact with potassium dichromate some twenty-four hours before use with solutions containing potassium dichromate and chromate. It was not practicable to check the electrode each time before making an estimation of the pH of a sample of the reaction mixture. This "drift" will there-

fore introduce a small uncertainty into the pH values recorded during the course of a reaction, but it is too small to affect materially the main conclusions drawn from the electrometric experiments.

Hughes (*loc. cit.*) and Dole (J.A.C.S., 1931, **53**, 4260) have failed to find any "mixed electrode" function such as that reported by Horovitz and Schiller. It is difficult to explain the above-mentioned "drift" as due to a "mixed electrode" function, since the electrode potential rises and then returns to its original value. Some temporary disturbance definitely appears to result if one allows an electrode to stand in contact with a given buffer over a long period, and then changes over to a solution of different ionic composition. It is hoped to reinvestigate this effect.

The Dichromate–Nitrite Mixture.—M/40 sodium nitrite, and M/80 potassium dichromate gave the following pH values. (The pH of the mixture increased overnight from 4·83 to 5·02 probably owing to loss of nitrous acid.)

	Eg.	pH.
M/80 $K_2Cr_2O_7$	0·202	4·20
M/40 $NaNO_2$	0·367	7·23
Mixture	0·237	4·83
M/20 $K.H.C_6H_4(COO)_2$	0·187	

These results were duplicated on the following day.

The Reaction.—Aniline (0·2 mol) in carefully purified methanol (50 cc.) was added to the well-stirred, cooled mixture containing the correct proportions of M/80 potassium chromate, M/40 sodium nitrite. Owing to the

rapid initial rise in pH the first readings were taken after each cc. of the aniline-alcohol mixture had reacted, and then after the addition of each 5 cc. In making a reading, 20 cc. of the solution were withdrawn, rapidly filtered from a small quantity of diazoaminobenzene, and, after recording the E.M.F., returned to the reaction mixture.

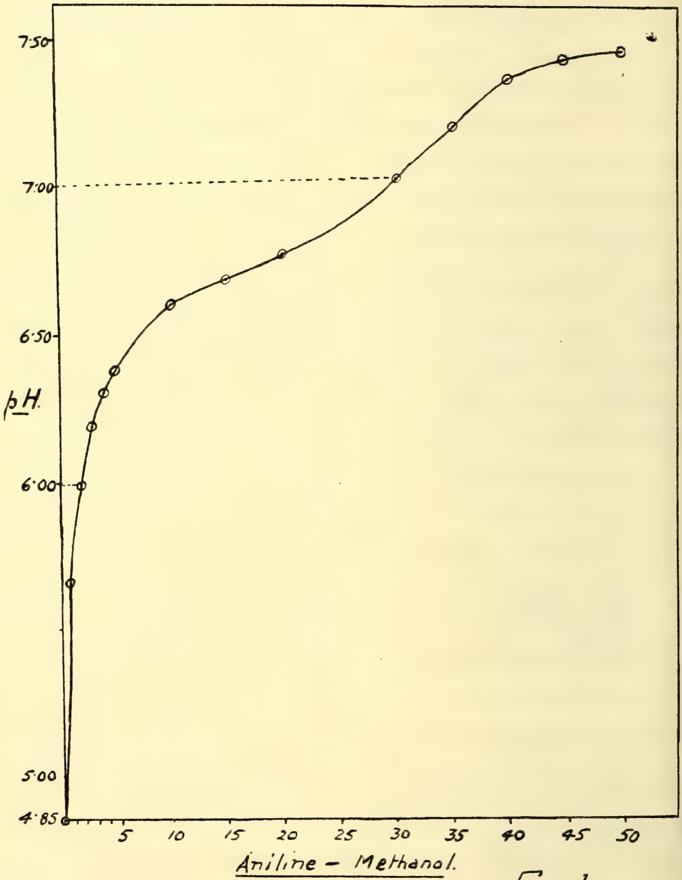


Fig. 1.

TABLE II.

Aniline-Alcohol. (cc.)	Eg.	pH.
0	0·243	4·85
1	0·289	5·65
2	0·308	5·97
3	0·319	6·16
4	0·326	6·29
5	0·330	6·35
10	0·343	6·58
15	0·348	6·67
20	0·353	6·75
25	0·361	6·88
30	0·367	7·00
35	0·378	7·18
40	0·386	7·33
45	0·389	7·38
50	0·391	7·41

E.M.F. of standard=0·187 volt.

By the addition of potassium-chromate (1 mol.) to the above mixture the initial pH was 6·33 and 7·13 after all the aniline had been added, the concentrations being as before, the reaction thus occurring within a 0·8 pH range (see Table III; Fig. 2).

TABLE III.

Aniline-Alcohol. (cc.)	Eg.	pH.
0	0·319	6·33
2	0·327	6·48
4	0·332	6·57
6	0·337	6·65
8	0·338	6·69
10	0·341	6·73
15	0·344	6·78
20	0·348	6·83
25	0·350	6·88
30	0·353	6·93
35	0·357	7·00
40	0·359	7·04
45	0·362	7·09
50	0·364	7·13

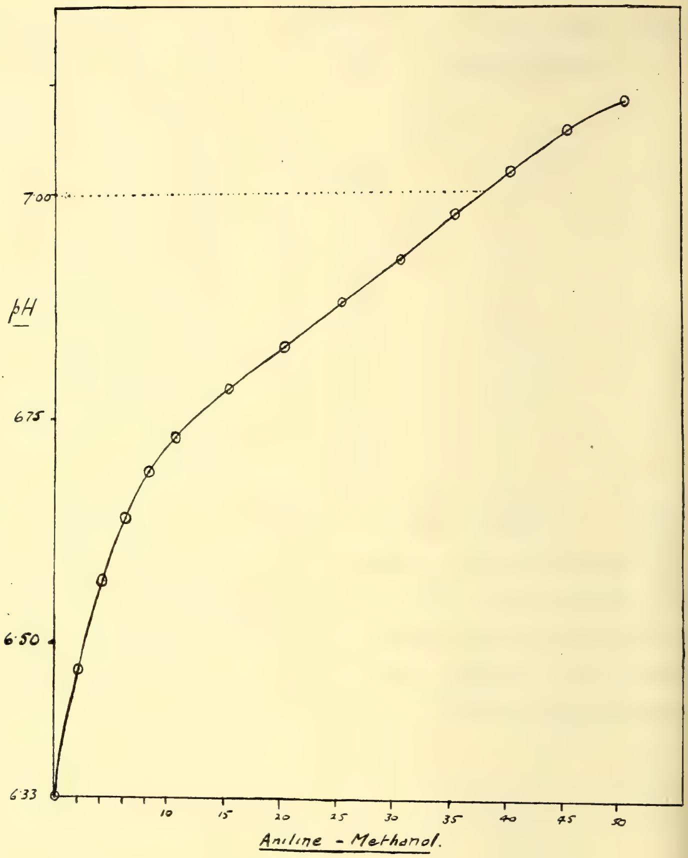


Fig. 2.

Table IV, Fig. 3, shows the course of the reaction when the original mixture was half-neutralised with sodium hydroxide (1 mol. for 1 mol. potassium dichromate), so that the initial pH condition was that of the half-way stage in the original reaction mixture. (About 1% more than 1 mol. sodium hydroxide was necessary to bring the pH exactly to 6·88.) The figures then approximate very closely to those in Table II:

TABLE IV.

Aniline-Alcohol. (cc.)	Eg.	pH.
0	0·355	6·88
2	0·357	6·92
4	0·360	6·97
6	0·363	7·02
8	0·366	7·08
10	0·372	7·17
12	0·376	7·25
15	0·382	7·32
20	0·383	7·36
25	0·385	7·41

In Table V (Fig. 4) are given the figures obtained during the titration of 0·1 M potassium dichromate with 0·1836 N potassium hydroxide. The form of the curve follows very closely that obtained by Britton (*loc. cit.*).

TABLE V.

Potassium hydroxide. (cc.)	Eg.	pH.
0	0·256	4·37
1	0·318	5·42
2	0·334	5·71
3	0·343	5·86
4	0·350	5·98
5	0·356	6·08
6	0·360	6·16
8	0·366	6·26
10	0·371	6·35
15	0·382	6·55
20	0·392	6·70
25	0·400	6·83
30	0·407	6·95
35	0·413	7·06
40	0·421	7·20
45	0·431	7·38
50	0·448	7·67
55	0·668	11·50

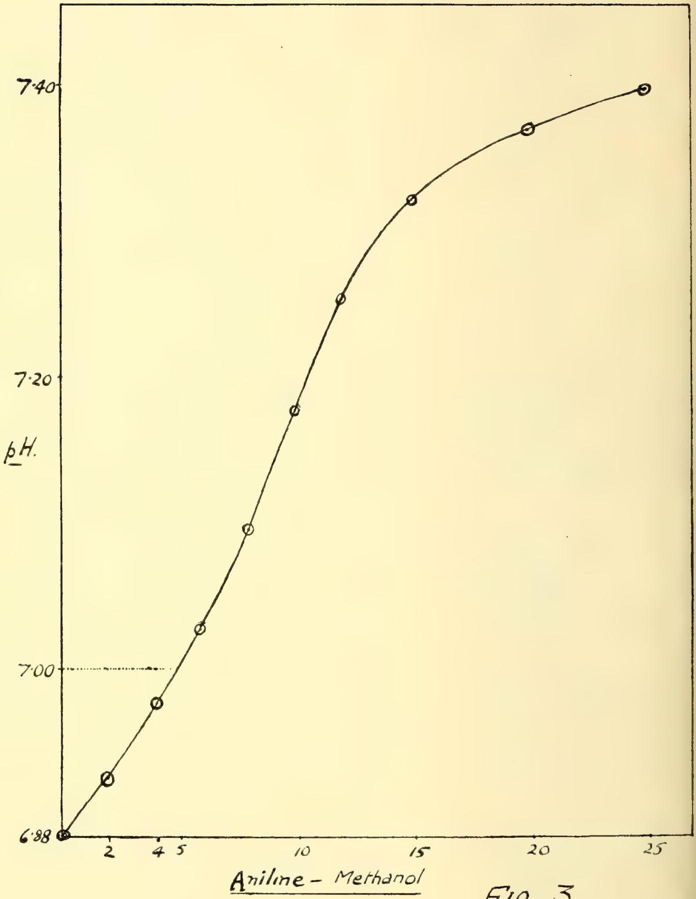


Fig. 3.

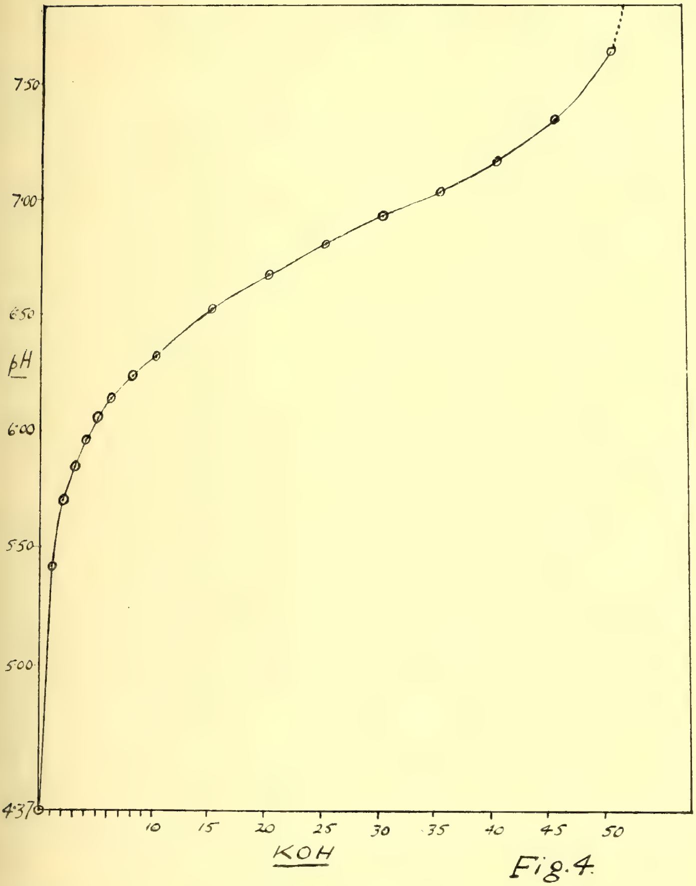


Fig. 4.

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THE ESSENTIAL OILS OF THREE SPECIES OF *GEIJERA* AND THE OCCURRENCE OF A NEW HYDROCARBON.

PART II.

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(*Read before the Royal Society of New South Wales, Sept. 7, 1932.*)

In a recent communication (*J. Proc. Roy. Soc. New South Wales,* 1930, **64**, 264) the isolation of a new hydrocarbon from the essential oil of *Geijera parviflora* was described. This hydrocarbon, for which we propose the name *geijerene,* is somewhat difficult to separate from linalool, with which it is associated in the oil, and the earlier analyses appeared to indicate the composition $C_{11}H_{18}$ or $C_{12}H_{20}$. Further investigation has shown this to be incorrect, geijerene being either $C_{11}H_{16}$ or $C_{12}H_{18}$. It is impossible to distinguish between these two formulæ by analytical methods and unfortunately the hydrocarbon yields no crystalline derivatives. We have, however, been able to show quite definitely by two distinct indirect methods that geijerene must have the composition $C_{12}H_{18}$.

In acetic acid solution in the presence of Pd-norite (see p. 336) geijerene is readily hydrogenated, the volume

of gas absorbed agreeing well with that required for three molecules of hydrogen assuming the formula to be $C_{12}H_{18}$. (H_2 = 4·260 l. calc. for $C_{12}H_{18}$ 4·386 l.; $C_{11}H_{16}$ 4·854 l.) It was further found that when geijerene was reduced catalytically and the reduction stopped after the absorption of two molecules of hydrogen, the *tetrahydrogeijerene* so obtained, gave on oxidation with either potassium permanganate or ozone formaldehyde (or formic acid) and a small quantity of a ketone, which from the analysis of the crystalline *semicarbazone*, had the composition $C_{11}H_{20}O$. It follows, therefore, that geijerene must have the formula $C_{12}H_{18}$.

Although we have carried out a large number of experiments we have been unable to obtain any evidence which would enable us to suggest a constitution for the hydrocarbon. Geijerene must be a monocyclic hydrocarbon containing three ethylenic linkages, one of which must be present as a methylene, $:CH_2$ group, which is probably attached to the ring, since the ketone, $C_{11}H_{20}O$, obtained on oxidation, did not give any bromoform when treated with sodium hypobromite. The ethylenic linkages are not conjugated since the hydrocarbon cannot be reduced by sodium in alcohol solution, nor does it react with maleic anhydride. This conclusion is supported by the evidence furnished by the determination of the molecular refractions of geijerene, tetrahydrogeijerene and hexahydrogeijerene, all of which show a decrement on the calculated value, as will be seen from the following figures:

	$[R_L]_D$ *Found.*	$[R_L]_D$ *Calculated.*	*Difference.*
Geijerene	53·33	54·015	− 0·68
Tetrahydrogeijerene ..	54·39	54·95	− 0·56
Hexahydrogeijerene ..	54·71	55·41	− 0·7

It is obviously not justifiable to draw any conclusions regarding the constitution of the hydrocarbons from these results, but attention may be directed to the fact that similar low molecular refractions have been recorded for hydrocarbons such as 3 : 3-dimethylpentane (– 0·20), 2 : 2 : 3-trimethylbutane (– 0·37) and 3-ethylpentane (– 0·24), all of which contain alkyl groups in close juxtaposition. It appears to us to be improbable that geijerene can contain a potential aromatic ring, since, when hexahydrogeijerene is heated with selenium, no hydrogen selenide is formed and the hydrocarbon is recovered unchanged. It is unlikely also that it contains a *gem*-dimethyl group, as neither on oxidation with potassium permanganate or with nitric acid is dimethylmalonic acid or *as*-dimethylsuccinic acid formed. We have investigated the oxidation of geijerene and of tetrahydrogeijerene both with ozone and with potassium permanganate under varied conditions, but apart from formaldehyde (and formic acid) and the small quantity of the ketone, $C_{11}H_{20}O$, referred to above, we have been unable to separate any recognisable products.

Our present experiments lead us therefore to the conclusion that geijerene, in addition to its abnormal composition, belongs to a new type of terpene hydrocarbon and it seems to us not improbable that it may contain a seven membered ring. Incomplete as these experiments are, we consider it desirable to place them on record in order to correct the erroneous composition previously assigned to the hydrocarbon. We hope that it may prove possible in a future communication to discuss the constitution of geijerene, but unfortunately its preparation in the quantity required for a detailed study is very laborious.

Experimental.

The hydrocarbon, which had been separated from linalool in the manner previously described (*loc. cit.*, p. 281), was further purified by repeated distillation over sodium when the following constants were observed:

b.p. 85°/17 mm., $d_{20^\circ}^{20^\circ}$ 0·8720, $n_D^{20^\circ}$ 1·4888, $[\alpha]_D \pm 0^\circ$

5·020 mgm. gave 16·280 mgm. CO_2, and 4·99 mgm. H_2O. C = 88·8, H = 11·0. $C_{12}H_{18}$ requires C = 88·9, H = 11·1 per cent.

Geijerene is a colourless mobile oil with a remarkable fragrant and distinctive odour. In acetic acid solution it gives with sulphuric acid a reddish violet coloration. As mentioned above, it is not reduced by sodium in alcoholic solution nor is it hydrated by sulphuric acid (3 per cent.). When it is treated with Aschan's reagent (sulphuric acid in ethereal solution) a diterpene, b.p. 210–215°/16 mm., is obtained. It does not react with maleic anhydride either in benzene solution or at the boiling point of the hydrocarbon. It is very readily attacked by potassium permanganate either in acetone solution or in aqueous alkaline solution, the oxidation being complete after the addition of permanganate corresponding to between 9 and 10 atoms of oxygen.

Under all the conditions investigated the products were a mixture of liquid acids which, after esterification, gave esters which distilled over a wide range. The presence of formic acid was established in the acids volatile in steam, but no acetone was formed when the oxidation was carried out in aqueous solution. The degradation is very profound since when the oxidation was carried out in alkaline solution, only 0·7 gram of acids were obtained from 5 grams of the hydrocarbon;

in acetone solution the yield was somewhat better, but the mixture of acids was equally complex. Oxidation with nitric acid gave oxalic acid as the sole product, whilst the hydrocarbon was not attacked by chromic acid in acetic acid solution.

Hexahydrogeijerene.

Geijerene (10 g.) in acetic acid (60 cc.) containing Pd-norite (2 g.; 0·2 g. $PdCl_2$) was shaken with hydrogen until the absorption of gas ceased. The hydrogenation was very rapid at first, but became slow after the addition of hydrogen corresponding to two ethylenic linkages had occurred. (H_2 absorbed 4·260 l. at 18° and 755 mm.; calc. $3H_2$ = 4·386 l.) The filtered solution was poured into an excess of potassium hydroxide solution, the hydrocarbon dissolved in ether, the ethereal solution dried and the solvent evaporated. The residual oil was distilled under diminished pressure, b.p. 95–97°/18 mm.; for analysis it was redistilled over sodium, b.p. 96°/20 mm., $d_{25°}^{25°}$ 0·8373, $n_D^{25°}$ 1·4577. 5·114 mgm. gave 16·035 mgm. CO_2, and 6·64 mgm. H_2O. C = 85·5, H = 14·5. $C_{12}H_{24}$ requires C = 85·7, H = 14·2 per cent.

Hexahydrogeijerene is a colourless mobile oil with a faint odour resembling somewhat that of the higher paraffins. It does not absorb bromine in chloroform solution nor is it attacked by potassium permanganate in hot acetone solution.

Tetrahydrogeijerene.

Geijerene (10 g.) in acetic acid (60 cc.) containing Pd-norite (0·5 g.; 0·05 g. $PdCl_2$) was shaken with hydrogen until the volume of gas absorbed corresponded

to the reduction of two ethylenic linkages. The filtered solution was poured into dilute potassium hydroxide solution and the hydrocarbon isolated in the usual manner.

Tetrahydrogeijerene, b.p. 95°/20 mm., $d_{25°}^{25°}$ 0·85058, $n_D^{25°}$ 1·4695, was a colourless oil having a pleasant lemon-like odour. 4·850 mgm. gave 15·319 mgm. CO_2, and 5·76 mgm. H_2O. C = 86·2, H = 13·2. $C_{12}H_{22}$ requires C = 86·8, H = 13·2 per cent.

In chloroform solution tetrahydrogeijerene readily absorbs bromine, but a crystalline bromide could not be prepared, the oil remaining on evaporation of the solvent decomposing with evolution of hydrogen bromide. Although the hydrocarbon boils very constantly, the slight discrepancy in the analytical figures recorded above and the fact that it yields a mixture of products on ozonolysis makes it somewhat doubtful if it is completely homogeneous. It is not improbable that it is contaminated with both hexahydrogeijerene and less hydrogenated products. The oxidation of tetrahydro-geijerene both with potassium permanganate and with ozone was studied under a variety of conditions but satisfactory results were not obtained. The following is a description of one experiment.

The hydrocarbon (6·7 g.) in acetone (100 cc.) was treated gradually with finely powdered potassium permanganate (12·5 g.), the temperature being maintained at 18–20°. The oxidation was very slow and required 4 days for addition and decolorisation of the permanganate. The manganese dioxide sludge was filtered off, well washed with acetone and the filtrate evaporated, the oil so obtained was distilled under diminished pressure

(16 mm.) when two main fractions were obtained: (i) b.p. 93–101° (3 g.), (ii) 101–130° (3 g.). The second fraction was dissolved in alcohol, mixed with an excess of semicarbazide acetate and allowed to stand for some days, when a crystalline *semicarbazone* (1 g.) slowly separated. This was purified by recrystallisation from methyl alcohol from which it separated in well formed hexagonal prisms, m.p. 163–164°.

4·840 mgm. gave 11·330 CO_2 and 4·43 mgm. H_2O. C = 63·8 H = 10·2.

3·246 mgm. gave 0·530 cc. N_2 at 22° and 758 mm. N = 18·45.

$C_{12}H_{23}ON_3$ requires C = 64·0 H = 10·2 N = 18·7 per cent.

From a small quantity of the semicarbazone (3 g.) the ketone was regenerated by treatment with oxalic acid; it was a colourless oil with a strong camphoraceous smell and it was readily volatile in steam. As mentioned above it did not yield any bromoform when shaken with an aqueous solution of sodium hypbromite.

The manganese dioxide sludge (see above) was extracted with hot water, the aqueous extract concentrated, acidified and extracted with ether, when a viscid oil (0·6 g.) remained on removal of the solvent. This did not crystallise or yield any crystalline derivatives and it was not further investigated.

The authors' thanks are due to the Government Grants Committee of the Royal Society for a grant which has defrayed a part of the cost of this investigation. They are indebted also to Imperial Chemical Industries for a research grant to one of us (J.L.S.).

NOTE ON THE INTERNAL STRUCTURES OF *BARRANDELLA* AND *SIEBERELLA*.

F. W. Booker, M.Sc.

(With Plate VI and two Text-figures.)

(Read before the Royal Society of New South Wales, Oct. 5, 1932.)

The occurrence of a new structure in the cruralia of certain galeatiform pentameroids was recorded in a paper published in 1926.[1]

This structure was found to exist in variously modified forms in the following Australian species:

Barrandella (*Barrandina*) *wilkinsoni*, Booker, 1926.
Barrandella (*Barrandina*) *minor*, Booker, 1926.
Sieberella glabra, Mitchell, 1920.

The structure was also found to exist in a specimen of *Sieberella galeata*, Dalman, from Wren's Nest, Dudley, England.

As the result of this discovery, an effort was made to obtain material from England and America for comparison with the Australian specimens. No American material has yet been obtained, but through the courtesy of Dr. F. Cowper-Reed, of the Sedgewick Museum, Cambridge, several specimens of *Barrandella linguifer*, Sowerby, and *Sieberella galeata*, Dalman, from Wren's Nest, Dudley, England, were made available.

These specimens were sectioned serially and the extra plate first identified in *Barrandina wilkinsoni*, was found in both species.

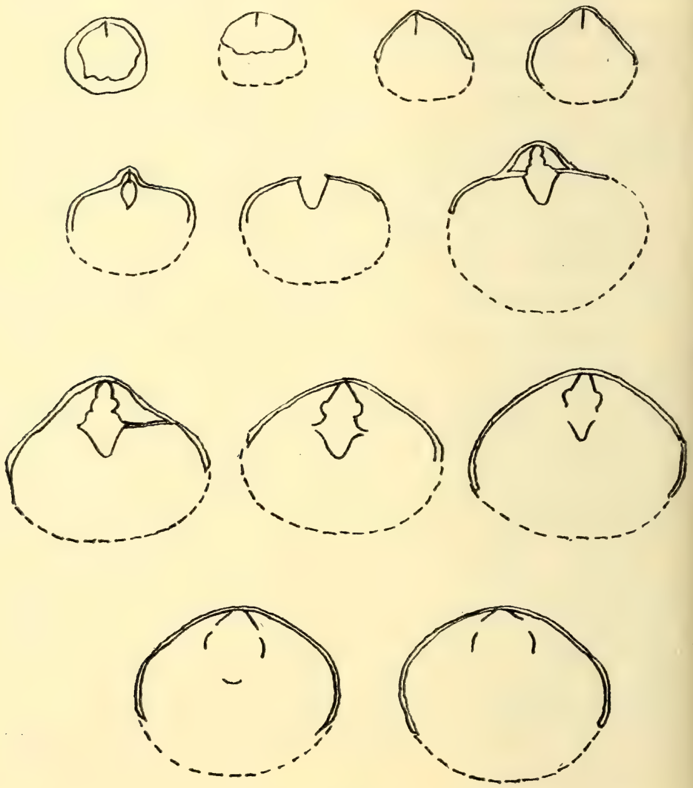
[1] Booker, F. W.: *Proc. Roy. Soc. N.S.W.*, lx, pp. 130-146, 1926.

The description of *Barrandella linguifer,* Sowerby, 1839, therefore requires modification as follows:

BARRANDELLA LINGUIFER, Sowerby, 1839.

(Plate vi, figs. 1, 2 and 6.)

Shell small sub-globose and inflated. The umbo of the pedicle valve is large, incurved, and much thickened. A median sinus is developed on the pedicle valve and the corresponding fold on the brachial valve. The sinus



Text-figure 1.
Barrandella linguifer, Sowerby. Serial sections.

is shallow and bounded by two slightly raised folds, while the fold is impressed with a faint median groove, i.e., the shell is uniplicate with a tendency to become biplicate. An area is absent in all cases and the surface of the shell is ornamented with a few growth lines only.

Text-fig. 1 shows a series of sections through the shell. From the figures it will be seen that the septum of the pedicle valve is very short indeed—shorter even than that of *Barrandina.* The spondylium extends forwards and is about one-third the length of the shell. The cruralium is supported for the whole of its length by two septa, which do not unite. The crural plates are only about half the length of the septa, and between septa and crural plates a pair of extra plates are intercalated.

The shape of the cruralium is as shown in Hall and Clarke, "Palæontology of the State of New York," Vol. 8, Part 2, p. 243, fig. 173, but for the fact that Hall has not realised the nature of the extra plates.

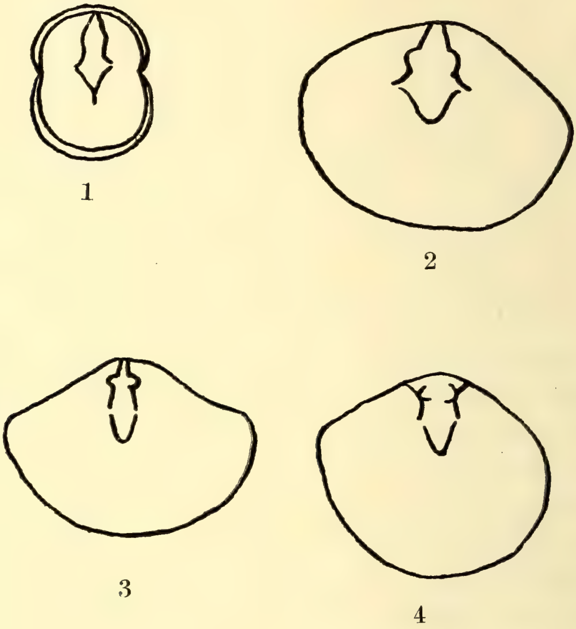
The spondylium shown in the figure does not agree with that of our specimen. Text-fig. 2 shows the internal structures of *B. linguifer, B. wilkinsoni, B. minor,* and Hall's figure 173, referred to above, in juxtaposition for comparative purposes.

The close relationship between *B. linguifer* and *B. wilkinsoni* is apparent at a glance, but it is possible that *B. minor* may need to be placed in a separate sub-genus.

A second specimen of *Sieberella galeata,* Dalman, from Wren's Nest, Dudley, sectioned serially gave identical results with those published in 1926,[2] and the description of this species should therefore be modified in accordance with the details of internal structure there published.

[2] *Loc. cit.,* pp. 142-144, 1926.

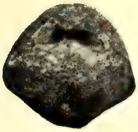
In a letter dated March 2, 1931, Dr. G. A. Cooper, of the Smithsonian Institute, states that the record of the occurrence of extra plates in the cruralia of *Barrandella* (*Barrandina*) is the first for this group of shells. He



Text-figure 2.

1. *Barrandella linguifer.* Hall and Clarke, Pal. New York, viii, pt. 2, p. 243, fig. 173.
2. *Barrandella linguifer.* Section of a specimen from Dudley, England.
3. *Barrandina wilkinsoni.*
4. *Barrandina minor.*

stated that he, Schuchert and Kozlowski have also detected the plates in serial sections, but he gives no references, and no published literature of theirs on this subject is available. Cooper also states that he finds no particular distinguishing features between *Barrandina*



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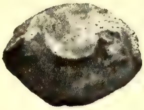

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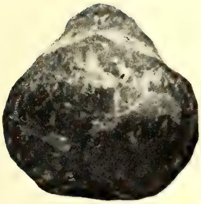

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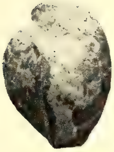

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6

EXPLANATION OF PLATE VI.

Figs. 1 and 2.—*Barrandella linguifer.* Two views showing the umbo and fold. × 1.

Figs. 3 and 4.—*Sieberella galeata.* Two views of a specimen from Dudley, England. × 1.

Fig. 5.—*Sieberella galeata.* Side view of a smaller specimen. × 1.

Fig. 6.—*Barrandella linguifer.* Side view of a larger individual. × 1.

and *Clorinda,* Barrande; but here again there is no material or literature available to decide the point either way. Barrande's figures (Systeme silurien, Vol. v, plates xxii, xxiv, cxix, and cxxxviii) show no resemblance between the two.

My thanks are due to Mr. W. S. Dun of the Geological Survey of New South Wales for his kindly advice. The sections and photographs used were prepared by Mr. G. Gabriel, lapidary to the Mining Museum.

NOTES ON THE MINERALOGY OF THE NARRABEEN SERIES OF NEW SOUTH WALES.

(A) The Heavy Mineral Assemblages.

(B) An Occurrence of Crystallised Quartz in a Sandstone from Bulli.

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(Communicated by Professor L. A. Cotton.)

(With Plates VII and VIII, and one Text-figure.)

(Read before the Royal Society of New South Wales, Nov. 2, 1932.)

Rocks of the Narrabeen Series, of Lower Triassic age, outcrop along the coast of New South Wales between Stanwell Park and Garie, and again between Collaroy and Tuggerah Lake. From the coast the outcrops swing inland along the slopes of the coastal ridge to the west of Kiama in the south, and along the hills south of the Hunter Valley to Murrurundi in the north. In the west they outcrop in the cliff sections of the Blue Mountain valleys, including the road at Mt. Victoria. The series has a maximum thickness of 1,740 feet measured at the Cremorne Bore, Sydney, but at the Blue Mountains the thickness is only about 300 feet.

The series is made up of sandstones, shales and sandy shales, with horizons of tuffs (partly redistributed), the most important being the chocolate shale which forms a very distinctive horizon near the top of the series. A

similar horizon of chocolate shale occurs near the base of the series.

(*a*) The Heavy Mineral Assemblages.

Originally it was hoped that a study of the heavy mineral content of the Narrabeen sediments would directly indicate their source. It was found, however, that a study of still older sediments (of Kamílaroi age) would be necessary before arriving at any definite conclusions regarding the source of the Narrabeen beds. Consequently this paper is intended only as a descriptive paper of the heavy mineral assemblages, but the writer hopes, at a later stage, to record the results of further investigations on the sedimentary rocks of Kamílaroi age and on their relation to the Narrabeen Series.

Localities Visited.—Rocks of Upper Narrabeen age (*i.e.*, above the upper chocolate shale horizon) were collected from Waterfall, Collaroy, Narrabeen, Turrimetta, Bilgola, Tudibaring, Avoca, Terrigal and Mt. Victoria. Specimens from Coal Cliff and Stanwell Park (south), and Toowoon Bay and Tuggerah locality (north) are from near the base of the Narrabeen series. From Garie and Bulli (south), Wamberal and Wyrrabalong (north), and Blackheath and Katoomba (west), specimens from intermediate depths were obtained.

Method of Examination.—The specimen to be examined was crushed in an iron mortar with an iron pestle. In crushing, grinding motion was avoided. The crushed rock was sieved, the fineness of the sieve used depending on the grainsize of the specimen. It was then weighed, and, where possible, from 500 to 1,000 grams of material were treated. Sometimes, however, a smaller weight was prepared. The rock sand was carefully panned, but

the panning process was not carried right to the end. The final separation was effected by heavy liquids. Sometimes boiling in dilute hydrochloric acid was necessary to remove iron oxides before complete washing and heavy liquid separation.

At first, for the separations, cadmium borotungstate was used in a Brögger funnel or a conical separating funnel. The separations thus made were quite good, but this method was abandoned as the cadmium borotungstate is very viscous, besides being dark in colour, and consequently separations were very slow.

Bromoform (sp. gr. about 2·9) proved to be the most satisfactory liquid to use. The bromoform can be used successfully in a conical separating funnel, or, as the writer prefers, in small evaporating dishes. In the latter case the liquid with the floating light fraction can be carefully poured from the heavy minerals, and a fairly pure separation thus effected. The vessels used are washed with benzol and the washings preserved for the recovery of the bromoform. This method is quick and efficient. The heavy minerals, thus concentrated, were weighed and the approximate percentage of the heavy mineral content was calculated. Finally, an electromagnetic separation was made into a magnetic and a nonmagnetic fraction.

For examination under the microscope the grains were immersed in refractive index liquids. Monobrombenzol (R.I. 1·55) proved specially satisfactory. This is slowly volatile, but gives time for examination of the grains before evaporation. The grains can thus be recovered, subjected to other R.I. liquid tests if necessary, or preserved in sample bottles for future reference. Permanent mounts of selected grains were made in xylol balsam.

In the examination of the chocolate shale the usual method was not adopted. After crushing and sieving, it was seen that the usual panning process would be useless, since all the grains were so heavily coated with iron oxide. Only a small quantity (50 grams) of the chocolate shale was treated. The grains were ground under water in an agate mortar with a rubber-covered pestle. This prevented, to some extent, fracturing and absolute powdering of the grains. The loose, soft iron oxide was removed after repeated grinding and boiling in dilute hydrochloric acid. The cleared grains were then separated and examined.

Thin sections were prepared for a general microscopic study of the specimens, and for a rapid survey of the light constituents.

Description of the Heavy Minerals.

The following heavy minerals have been recognised in the Narrabeen sediments:

Cubic—
- Chalcopyrite.
- Galena.
- Garnet.
- Magnetite.
- Pyrites.
- Picotite.
- Spinel.

Tetragonal—
- Anatase.
- Rutile.
- Zircon.

Hexagonal—
- Apatite.
- Calcite.
- Ilmenite.
- Siderite.
- Tourmaline.

Orthorhombic—
- Barytes.
- Brookite.
- Hypersthene.

Monoclinic—
- Biotite.
- Chlorite.
- Monazite.
- Muscovite.

Limonite and hæmatite, derived from iron-bearing minerals, and leucoxene, from ilmenite, also occur.

Chalcopyrite.—This is present in only four of the specimens examined, *viz.*, tuff about one foot above the upper chocolate shales at Bilgola, basic tuff from Garie

about fifty feet below the upper chocolate shale horizon, and two sandstones from Terrigal. In no case is it abundant, several grains only being observed in each sample. In size they are 0·1 mm. or less across. In reflected light they show a brassy or golden colour with metallic lustre and vivid red and purple tarnish.

One of the Terrigal samples shows the chalcopyrite to be in association with a deep red opaque mineral, the latter apparently either coating the chalcopyrite or forming complete pseudomorphs. Several aggregates of small red crystals were observed. The individual crystals were tetrahedral, resembling crystals of chalcopyrite and also showing a diagonal striation characteristic of chalcopyrite[(5)] (p. 80). Microchemical tests with nitric acid showed both minerals to be insoluble, proving the red to be hæmatite, and confirming chalcopyrite. The hæmatite may be either a decomposition product of chalcopyrite[(5)] (p. 82), or else a secondary coating.

In the remaining three samples the chalcopyrite occurred as irregular grains and showed no crystal form.

Galena.—This was observed in sandstones from Mt. Victoria. Only a few grains were found, these being present as cleaved fragments. Cubic cleavage is well shown, the fragments having "stepped" edges. The galena is black and opaque in transmitted light, but shows a grey colour and metallic lustre in reflected light. In size the grains average 0·15 mm. by 0·2 mm.

Garnet is present only in the sediments north of Broken Bay, and was absent, too, from the six specimens examined from the Blue Mountains. It formed only a rare constituent usually, but was slightly more frequent in material from Toowoon Bay and Terrigal.

Colourless, pale pink and brownish-pink grains occur, the very pale pink variety being most frequent. The grains are usually very irregular with a hackly fracture, or, rarely, a sub-conchoidal fracture. Some are inclined to be flat, or platey, due to the development of the dodecahedral cleavage, while a few rather rounded grains were observed from Toowoon Bay and south of The Entrance, Tuggerah. The (211) faces were recognised in a crystal from Toowoon Bay.

Garnet is recognised by its weak magnetism, very irregular fracture, vitreous to slightly resinous lustre, high R.I., and its isotropism.

Magnetite has a wide distribution, but is generally scarce in most of the concentrates. It is very abundant, however, in the tuff from Garie, where it forms about 30% of the total concentrate. Usually it occurs as irregular, dull or submetallic black grains, averaging 0·1 mm. across. Some rounded grains and octahedral crystals occur more rarely. Alteration to hæmatite and limonite is frequent. The magnetite is separated from the concentrate by a horse-shoe magnet.

Pyrites.—This is essentially a rare constituent, a few grains occurring in samples from Turrimetta, Bilgola, Hole in the Wall, Coal Cliff and Mt. Victoria. It was more frequent in the Hole in the Wall sandstone than in the other specimens. It occurs, usually, as irregular brassy yellow grains averaging 0·1 mm. across. Cubic cleavages are observed in some of the fragments. In the Bilgola tuff concentrate it is found in composite grains with quartz, and appears to be encrusting. In a coarse sandstone from Turrimetta some pyrites showed definite crystal form, pyritohedra being recognised, and also some

aggregates showed tiny crystal faces. Some grains show oxidation to brown limonite.

Picotite is present in all the concentrates obtained, but the proportion is very variable. It is most abundant in the concentrates from Coal Cliff and Stanwell Park, where it forms from 40% to 50% (by number) of the heavy mineral content. It is also common in the concentrates from Wyrrabalong and Toowoon Bay, but somewhat less frequent in specimens from lower levels of the exposures at Katoomba and Blackheath, and the Terrigal area. In the upper Narrabeen beds between Collaroy and Barrenjoey, at Waterfall and Mt. Victoria the proportion of picotite is much lower.

The picotite is black in colour, but rarely, on the thin edges, a brown or deep green translucency may be obtained. The lustre is vitreous, or less commonly submetallic. Fractured grains show excellent conchoidal fracture. The mineral is moderately magnetic. It occurs frequently as perfect little cubic crystals. The octahedra alone are usually developed, but in many cases they are combined with the dodecahedra, and less commonly the cube faces are developed. Many crystals are worn so as to be almost spherical. Twinned crystals are common (Plate VII, 18). Single twins are specially common, but occasionally chains of three crystals have been observed. The size varies from about 0·05 mm. to 0·2 mm. Some of the octahedra of the larger crystals show triangular markings, or etch figures.

In most concentrates some crystals are present, but grains showing no crystal faces may be difficult to distinguish from ilmenite. Bead tests have been made in all doubtful cases, and a good emerald green colora-

tion of the borax or microcosmic salt beads has proved the presence of chromium.

Also there were some doubts as to whether the mineral should be called picotite or chromite, since actually a chemical analysis is necessary for a final decision, and this was impracticable. The vitreous lustre and the presence of etching, however, are more characteristic of picotite and so the mineral was accordingly so named. There may be types intermediate between picotite and chromite, or some of the chrome-bearing grains may be chromite.

Spinel.—This mineral is represented by only one grain in each of the Katoomba and The Entrance samples. It is light, bright green with a vitreous lustre, very high R.I., and it is isotropic.

Anatase was found in practically all the concentrates. It is particularly common in samples from between Tudibaring and The Entrance, Tuggerah, and also in several samples from Stanwell Park. In other concentrates it was a rare, but fairly constant, constituent. It occurs as irregular angular grains, as aggregates of tiny crystals or as individual crystals. The colour varies from almost colourless, through light yellow to deeper brownish yellow. Pale blue, medium blue and greenish blue anatase occur, but are not so common as the yellow varieties. Anatase may be quite clear, slightly cloudy, or opaque. The lustre is resinous in some of the opaque grains, but more frequently it is adamantine. Square or rectangular tabular crystals with bevelled edges are very common. This characteristic shape is due to the good development of c (001), and subordinate development of p (111). Diagonal striations, or two sets of striae at right angles parallel to the crystal edges, may

be present on the basal plane. Parallel intergrowths of tabular crystals of varying size are common, giving rise to "stepped" edges as in Pl. VII, 1 and 2. The basal planes of tabular crystals appear isotropic and give good uniaxial negative interference figures.

Elongated bipyramidal crystals (Pl. VII, 3) showing strong development of (111) are less frequent than those of tabular habit, and almost invariably they have a horizontal striation.

Rutile.—This mineral is widely distributed but is not abundant in any of the concentrates prepared. In colour it varies from yellow, through brownish and reddish yellow, to a very deep reddish brown and red. Grains showing crystal faces are rare. Prism faces are more often preserved than terminal faces although 1st and 2nd order pyramids have been recognised. A few examples of geniculate twinning have been observed.

In shape the grains are irregular, or, more frequently, vary from oval grains to elongated worn prismatic or rod-shaped grains, whose ratio $\frac{\text{length}}{\text{breadth}}$ may reach $\frac{6}{1}$. Rutile may cleave parallel to (110) or (100) prisms, and resulting flat fragments may show traces of the (111) cleavage. The surface of the grains is usually rough and pitted. Elongated grains frequently have a shallow grooving or striation parallel to the prisms. Fractured surfaces have a vitreous lustre and the fracture is sub-conchoidal. Some grains are weakly pleochroic, the position of maximum absorption being parallel to the vibration direction of the polariser. Rutile is distinguished by its colour, lustre, straight extinction, and very high R.I.

Zircon is invariably present and in the sandstones may form as much as 90% of the heavy mineral content. It rarely forms less than 50% of the concentrate. Rounded grains and perfect crystals are usually present together in the one concentrate. Perfect tetragonal crystals are very common. The forms most commonly developed are the unit prism and unit pyramid, and the 2nd order prisms and pyramids; the pyramid (311) is fairly common, and (331) less common. The basal plane (001) is rarely seen. Often the crystals show pyramidal terminations on one end only. They may be fractured or cleaved parallel to the pyramid (111).

Zircons are usually rather elongated parallel to the prisms. The maximum values for the ratio $\dfrac{\text{length}}{\text{breadth}}$ are 9 and 8, observed in zircons from Tudibaring and Mt. Victoria respectively. The largest zircon observed (from Tudibaring) measured 0·5 mm. × 0·2 mm. The smallest are typical of the very fine sandstones and sandy shales and may average as small as 0·05 mm. in length in these rocks. The average length of the zircons is about 0·15 mm. and the average value for the ratio $\dfrac{\text{length}}{\text{breadth}}$ is 2. Generally the zircons from Stanwell Park, Coal Cliff and the Terrigal district show larger development than those from other localities.

Rounding is common with the production of ellipsoids or spheres.

Most of the zircons are clear and colourless. Some are light yellow and clear, and a few are deeper yellow and tend to be translucent. A concentrate from a Terrigal sandstone is peculiar in showing one mauve zircon and several green zircons. The green zircons

were slightly pleochroic having maximum absorption parallel to the vibration direction of the polariser.

Inclusions are very common. These are usually indeterminate, but tiny zircon and rutile crystals have frequently been recognised. Tubular or rod inclusions may often be found parallel to the prisms, either along the axis or otherwise, and may extend practically the whole length of the crystal. The tubular inclusions may be irregular and branching. The smaller inclusions are centrally placed, arranged parallel to the prisms and in zones, or they may be scattered irregularly through the crystal. Sometimes the inclusions are so very tiny and dust-like and so crowded that they give a deep grey coloration to the zircons. Other crystals are turbid because of the dust-like inclusions.

Zoning is frequent even in the small crystals, although it is more characteristic of the larger ones (Plate VIII, 1 and 2). The zone lines generally follow the contour of the crystal, except at the ends where they become rounded.

Many of the perfect zircon crystals have been protected from abrasion during transport by other minerals.

Apatite is practically restricted in occurrence to concentrates from the north, being most common at Toowoon Bay. A concentrate from a Bulli sandstone contains several grains of apatite.

Generally it occurs as colourless, transparent, vitreous elongated grains, remnants of long prismatic crystals. The crystal edges are worn, and the ends rounded. The grains may be doubly terminated although frequently there has been breaking along the basal parting. The R.I. is medium, between 1·63 and 1·639. Between crossed nicols apatite shows 1st order grey or

yellow interference colours (depending on the thickness of the grain), and it has negative elongation. Extinction is straight. Cross sections give uniaxial negative interference figures, but satisfactory sections are rarely available. This determination was confirmed by a microchemical test on several isolated grains. The grains were dissolved in nitric acid, ammonium molybdate in aqueous solution was added, resulting in the precipitation of yellow ammonium phospho-molybdate.

In concentrates from Toowoon Bay and Wyrrabalong several grains of brown apatite were recorded, the depth of colour varying in different grains. These are rounded prismatic in shape, with domed ends, or broken along a parting, or fractured across. Pleochroism varies in strength, some being markedly pleochroic from a light yellowish brown to a deep reddish brown, E > O. Iddings[14] (p. 524) records a weak pleochroism for coloured apatite. The strength of the pleochroism in these grains would be due to the thickness of the grains which is sufficient to give a bright yellow interference colour.

A microchemical test for the brown grains confirmed the phosphate.

Calcite and Siderite.—These minerals, where present, were detected by their reaction with hydrochloric acid or by examination of rock micro-sections. Their mode of occurrence will be discussed in a later section of the paper.

Ilmenite is present in most of the concentrates, but rarely is it abundant. At Wyrrabalong and Toowoon Bay it is more abundant than elsewhere. It usually occurs as rounded or irregular grains, but sometimes

crystal outline can be determined. It has a submetallic lustre. Alteration takes place to leucoxene.

Tourmaline is present in all the concentrates obtained, in slightly greater proportion than rutile. The colour is very variable. Most commonly it has a medium greenish-brown colour, but other shades are also noticed, *viz.*, almost colourless, light green, light brown, reddish brown, purplish brown, and a dark greenish-brown, while usually several light blue (sometimes dark blue) grains are present in the concentrates. The Wyrrabalong concentrate has parti-coloured or colour zoned brown and green tourmaline. The lustre is resinous or vitreous, and the grains are transparent or translucent.

Sharply angular crystals are scarce. Frequently considerable rounding has taken place smoothing off the crystal edges till eventually the grains have become ellipsoidal or spherical. Prismatic grains are the most abundant. Rarely the rhombohedra are preserved. The grains may have straight terminations along a basal parting or they may be fractured. The fracture is sub-conchoidal.

The surface may be smooth, or rough and striated. The blue variety is usually heavily striated, and the grains are angular and fragmental, sometimes exhibiting prism faces.

Numerous bubble inclusions are present in the greenish brown variety, but inclusions have not been noted in the blue.

Pleochroism is strong in the greenish brown grains, $E < O$. This is an important diagnostic property. The pleochroism of the blue tourmaline is very weak or apparently absent.

The R.I. is medium, and prismatic grains show straight extinction.

The average size is about 0·2 mm. × 0·1 mm.

Barytes is present in seven of the concentrates examined, *viz.*, from Stanwell Park (where it formed about 50% of the heavy minerals), Garie and from the Terrigal-Wyrrabalong area. It is colourless or white, and the lustre is vitreous or waxy. The R.I. is medium, slightly less than 1·642. The double refraction is weak and extinction is straight.

In the Stanwell Park and Garie concentrates it occurs in stumpy grains which reach 0·2 mm. in length, and which, although smoothed on the surface, show traces of crystal faces. The crystals are shortened parallel to c, and elongated parallel to b. High 1st order colours are shown between crossed nicols. Several good biaxial positive interference figures were obtained.

In the other concentrates the barytes is present as cleavage plates, the mineral cleaving perfectly parallel to (001). The resultant cross sections are idiomorphic, usually either six or eight sided. Angles measured from several of these sections showed that they were bounded by the prisms a, b and m. Such sections exhibit 1st order grey and yellow interference colours. Biaxial figures could be determined, but the sign could not be obtained. Alteration shows up usually at the edges, and quite often in a square or rectangular area along the axis of the crystal.

Brookite is a very rare constituent, found only in concentrates from Avoca, Terrigal, Toowoon, Wyrrabalong and Mt. Victoria. It is always associated with anatase and rutile.

Brookite is translucent with a resinous lustre. It is pale yellow, greenish yellow, or deep amber yellow in colour, and occurs as irregular plates flattened parallel to the (100) face. The presence of a very narrow b (010) face has been noted in several grains, while c (001) and brachydomes have only been observed in one fractured crystal from Terrigal. Vertical striations are often seen on (100) face. With the low power of the microscope the mineral shows straight extinction, but with high power it is seen that the plates do not extinguish completely. They show a big range of interference colours during a rotation of the stage, never becoming completely dark. The double refraction is very high, and the interference colours are high order pinks, reds, greens and neutral shades.

Excellent biaxial positive interference figures are obtained from (100) plates, and these show very strong dispersion.

Brookite is weakly pleochroic, the position of maximum absorption being parallel to the vibration direction of the polariser. The R.I. is very high.

Hypersthene. Only one grain of this mineral was found in a sandstone from south of The Entrance, Tuggerah. It was an irregular grain showing evidence of two cleavages at right angles. It showed vertical striations, and was faintly pleochroic from very light green to very light pink. In transmitted light it was almost colourless.

Biotite is not frequently present and is never abundant. In the sandy sediments where it occurs it forms irregular cleavage flakes, which are light brown in colour. In the basic tuff at Garie it occurs in very well defined hexagonal basal sections and also as irregular forms.

The hexagonal sections are very dark greenish brown and have a submetallic lustre. These sections reach 0·3 mm. across.

Iron oxide inclusions are present in some, and alteration to chlorite has been noticed.

Chlorite is rare as a heavy mineral. It is noticed in several microscope slides in the rock cement, but only in the Garie concentrate did it form an important constituent. In this it formed hexagonal pseudomorphs after biotite. The colour varied from light to dark green.

Muscovite is common. Much muscovite is lost by panning because of its flaky nature. In the concentrates it occurs as colourless cleavage flakes with irregular outlines. These show high order interference colours, and low R.I. Muscovite is also noted in the microscope sections.

Monazite has been noticed only in the Terrigal-Pelican Point locality, where it is a rare constituent. It occurs as rounded or ellipsoidal cloudy yellow grains, with resinous lustre. These show a small extinction angle, a high R.I., and usually high order neutral interference colours. Weak pleochroism is noticed in some grains.

Discussion and Significance of the Heavy Minerals Present.

A study of Tables I and II shows that the percentage of heavy minerals in the Narrabeen sediments is variable but is always low.

The heavy minerals present, for purpose of discussion, may be grouped into three divisions:

(1) The stable minerals, including zircon, rutile, tourmaline, magnetite, ilmenite and picotite.

LOCALITY	TYPE OF SEDIMENT	Approx. percentage of heavy minerals	Chalcopyrite	Magnetite	Pyrites	Picotite	Anatase	Rutile	Zircon	Apatite	Calcite or Siderite	Ilmenite	Tourmaline	Barytes	Biotite	Muscovite	Quartz	Felspar
			Cub.				Tet.			Hex.				Orth	Mono.			
Bulli	*Sandstone*	·09		r		c	r	r	a	s			c			p	P	p
Coal Cliff	*Tuffaceous sandstone*	·03			s	a	r	s	a		p		r			p	P	p
Coal Cliff	*Calcareous tuff*	·01				r		c	a		P	r	r				p	
Stanwell Park	*Sandstone*	·02				C		r	a		p		r				P	
Stanwell Park	*Tuffaceous sandstone*	·03		s		C	c	r	a				c				P	
Stanwell Park	*Sandstone*	·01		r		C	c	s	c			s	r	a			P	
Stanwell Park	*Sandstone*	·02				r	s	r	a				c			p	P	p
Garie	*Basic tuff*	·08	s	C		c		r	c			r	r	c	p		p	
Waterfall	*Sandy shale*	·01				r		C	a				r			p	P	
Collaroy	*Fine sandstone*	·09		s	s	c	s	c	A				c		p	p	P	p
Narrabeen	*Sandy shale*	·02		s		C	r	r	C				c			p	P	
Turrimetta	*Sandstone*	·02			s	r	s	c	A				c				P	
Turrimetta	*Fine sandstone*				s	r	r	c	A			s	c				P	p
Turrimetta	*Coarse sandstone*				r	r	r	c	a				C				P	p
Bilgola	*Fine sandstone*	·02				r	s	r	A				r			p	P	
Bilgola	*Chocolate shale*					p_c		p_c	p_c				p_c				P	p
Bilgola	*Grey tuff*		s	s	r	c			s			a	r				P	
Hole in the Wall	*Sandstone*	·03			r	c		r	a			r	c			p	P	p

Table 1.—Summary of Mineral Distribution.

The following symbols and approximate percentages refer to the heavy mineral concentrates:

A = very abundant ($\eqslantgtr$ 75%), a = abundant ($\eqslantgtr$ 45%, but < 75%).
C = very common ($\eqslantgtr$ 25%, but < 45%), c = common ($\eqslantgtr$ 5%, but < 25%).
r = rare ($\eqslantgtr$ 1%, but < 5%), s = scarce (< 1%).
p_c = present in concentrate, but proportions not determined.

The following symbols refer to the presence of minerals as determined by microscope slides:

LOCALITY	TYPE OF SEDIMENT	Approx. percentage of heavy minerals	Chalcopyrite	Galena	Garnet	Magnetite	Pyrites	Picotite	Spinel	Anatase	Rutile	Zircon	Apatite	Ilmenite	Tourmaline	Barytes	Brookite	Hypersthene	Biotite	Monazite	Muscovite	Quartz	Felspar
						Cub					Tet.			Hex			Orth.			Mono.			
Little Beach	*Sandstone*	·1			r	r		r		r	r	a			c						p	P	p
Tudibaring	*Sandstone*	·05			r	r		r		c	r	a		r	c				nd	s	nd	P	nd
Avoca	*Sandstone*	·07			s			c		c	r	a			c	c	s		nd	s	nd	P	nd
Avoca	*Fine sandstone*	·03						c		c	r	C		r	c	c				s	p	P	p
Terrigal	*Sandstone*	·03			r			c		c	r	a	r		c				p	r	p	P	p
Terrigal	*Sandstone*		s		r	r		r		c	r	a		r	c	r			p		p	P	p
Terrigal	*Green sandstone*	·1	s		r			r		r	r	a		c	r		s			r		P	p
Wamberal	*Green sandstone*	·02			r			c		c	r	a	r	r	c				nd		nd	P	nd
Wyrrabalong	*Tuff with choc. shale*	·08			s	r		c		r	r	a	r	c	r		s					P	p
Toowoon Bay	*Tuff below choc. shale*	·06			r	r		c		r	r	a	c	c	r							P	p
Toowoon Bay	*Green tuff*	·05			r	c		c		r	r	a	c	r	r							P	p
The Entrance	*White sandstone*	·01			r			r	s	c	r	a		r	c			s		s		P	p
Katoomba	*Fine sandstone*	·05				r		r	s	r	r	A		r	c							P	
Blackheath	*Fine sandstone*	·03				r		r		r	r	A		r	c				nd		nd	P	nd
Blackheath	*Fine sandstone*	·1				r		c		r	r	A		c	c							P	
Mt. Victoria	*White shale*	·01						r		r	r	A			c		s		nd		nd	P	nd
Mt. Victoria	*Fine sandstone*	·05		s				r		s	r	A			r							P	p
Mt. Victoria	*Coarse sandstone*	·03		s			s			s	c	A			r							P	p

Table 2.—Summary of Mineral Distribution.

The following symbols and approximate percentages refer to the heavy mineral concentrates:

A = very abundant ($\geqq 75\%$), a = abundant ($\geqq 45\%$, but $< 75\%$).
C = very common ($\geqq 25\%$, but $< 45\%$), c = common ($\geqq 5\%$, but $< 25\%$).
r = rare ($\geqq 1\%$, but $< 5\%$), s = scarce ($< 1\%$).
p_c = present in concentrate, but proportions not determined.

The following symbols refer to the presence of minerals as determined by microscope slides:

P = present in large quantity, p = present in small quantity.
nd = presence not determined (microscope slides were not made).

(2) The less stable minerals, including galena, garnet, spinel, apatite, hypersthene, biotite, muscovite and monazite.

(3) (*a*) The authigenic minerals, including chalcopyrite, pyrites, anatase, brookite, some rutile, leucoxene, calcite, siderite and barytes.

(*b*) The secondary minerals, including chlorite, muscovite, hæmatite and limonite.

(1) *Zircon, tourmaline and rutile,* as primary derivatives, are characteristic of acid or intermediate igneous rocks and certain metamorphic types[18] (p. 84, p. 80, p. 73). These are ubiquitous minerals and may survive more than one erosion cycle, so they give very wide possibilities for the origin of the sediments. But the presence of rare minerals such as green and mauve zircons, as found at Terrigal, must certainly limit the range of possibilities and, it is hoped, may give a definite clue to the parent rocks of the Narrabeen beds.*

The *picotite* which is a constant constituent must have been derived originally from some ultra-basic mass. Such masses, apparently capable of supplying the picotite, are:

(*a*) The Great Serpentine Belt, in which large chromite deposits are recorded[1] (pp. 680-681, p. 705).

(*b*) Ultra-basic rocks at Lucknow. A natural concentrate from Lucknow (kindly lent by Mr. L. L. Waterhouse, B.E., to the author), consisting mainly of chrome garnet, was found to contain a number of small crystals of picotite.

(*c*) The Gundagai-Berthong serpentines, in which picotite and chromite are recorded[15] (p. 21, p. 22) [16] (p. 63).

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* See Note, page 371.

There can be little doubt that the picotite has been derived directly or indirectly* from these ultra-basic masses, or perhaps from previous extensions of these masses.

(2) The less stable minerals occur locally, being characteristic of certain areas.

Galena was found in small quantity in sandstones from Mt. Victoria. It is probably derived as a detrital mineral from the Devonian batholith a few miles west of the western edge of the Narrabeen beds. Large deposits of galena occur at Yerranderie and Sunny Corner, and numerous smaller occurrences are known in the pneumatolytic phases of the intrusion. Galena is rare as a detrital mineral, but since Mt. Victoria is near the source of the material little transport would be required to bring it to its present position. Chemically galena is fairly stable, but the softness and cleavage of the mineral usually cause its disintegration.

It is possible, though improbable, that the galena is of secondary origin, in which case the lead sulphide would be precipitated directly from water containing lead sulphide in solution or from interaction of a lead compound solution with sulphur-bearing solutions. The original source of the lead would again be from the pneumatolytic deposits in the Devonian batholith to the west.

Garnet, apatite and monazite are characteristic of sediments from the northern section, and, except for several grains of apatite which were noted in a sandstone from Bulli, these minerals are absent from other concentrates examined. The brown apatite, which is present

* See Note, page 371.

in the concentrates from Wyrrabalong and Toowoon Bay, should prove a valuable index mineral.*

Hypersthene was found in a sample from The Entrance, while *spinel* was found only at The Entrance and Katoomba.

Biotite and muscovite have but little significance as index minerals.

Thus the important index minerals are seen to be practically restricted to the northern Narrabeen sediments.

(3) *Iron pyrites* is present in small quantity in eight of the concentrates studied. Usually it is present as irregular grains, but pyrites from Turrimetta shows some crystal form, suggesting formation *in situ.* All the pyrites in the Narrabeen sediments is probably authigenic, resulting from the action of sulphuretted hydrogen on iron compounds, the sulphuretted hydrogen being derived by bacterial action on organic material in the lake of deposition.

That dyke intrusions may introduce pyrites into the surrounding rock was considered as a possible method of origin for the pyrites. A dyke intersects the Hole in the Wall headland, but, at other localities from which pyrites bearing specimens were obtained, no dykes which could introduce the vapours or solutions for the precipitation of the pyrites are known to the writer.

In the green sediments from the Terrigal-Tuggerah locality pyrites is absent, affording an illustration of the statement[19] (p. 114) that "in green rocks it tends to be rare or absent where the colour is due to chloritic products".

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* See Note, page 371.

The *chalcopyrite* is probably caused by the interaction of sulphur-bearing solutions, derived by bacterial action, with other copper compounds. Cupriferous tuffs have been reported from several horizons in the Narrabeen series[(8)] (p. 275). Usually the copper is present as native copper, or as the chloride as at Long Reef near Narrabeen. The horizon of tuffs bearing chalcopyrite at Bilgola corresponds to that showing traces of copper at Long Reef. The copper is thought to be derived from the disintegration of cupriferous ferro-magnesian minerals and subsequent precipitation from solution of copper salts.

Chlorite, as the alteration product of ferro-magnesian minerals, is very plentiful in the Garie cupriferous tuff and the Terrigal sandstones.

The Titanium Minerals.—The occurrence of *anatase* in perfect crystals, as individuals or as aggregates, indicates that the anatase is definitely authigenic. It is by far the most common authigenic titanium mineral present. The *brookite* shows no sign of transport, but sharp edges are noticed between the crystal faces (100 and 010) in the irregular grains examined. It, too, is authigenic. *Rutile* is present as both detrital and authigenic crystals or grains.

Ilmenite is present in most of the concentrates, and probably furnishes some titanium for the anatase, brookite and rutile. It is also possible that titaniferous biotite[(2)] (p. 24) or sphene, on disintegration, has liberated the titania which on crystallising has formed anatase.

Composite grains showing alteration from one titanium mineral to another were not observed in the Narrabeen concentrates.

Barytes.—The sharp idiomorphic character of the barytes marks it as being authigenic, since it is very soft ($H = 2 \cdot 5$ to $3 \cdot 5$) and any transport would quickly destroy its crystal edges and shape. Crystals of barytes occur in joints in the Narrabeen beds near Narrabeen, and rounded pebbles derived therefrom are found in the beach shingle at the same locality. Barytes has been recorded elsewhere in the Triassic from various localities [13] (p. 408), [21] (p. 131), [6] (p. 407).

Barytes is usually indicative of aqueous origin, and is most characteristic of lacustrine deposits. It may be precipitated by the intermingling of a solution of a barium compound (most commonly the chloride or the bicarbonate) with a solution of a soluble sulphate,[17] (p. 334), or it may be deposited directly from normal ground water[10] (p. 365). Barytes itself is "not entirely insoluble, especially in carbonated waters"[17] (p. 334).

It is commonly assumed that the barium which goes to form this mineral is liberated originally as barium oxide by the decomposition of felspar and mica, from which it is dissolved in the process of weathering.

But it is possible, however, that the barium is derived, not from felspars and micas, but from barium-bearing rocks such as limestones in which it is very likely to occur[17] (p. 334), or even from large barytes deposits. Even if the solubility of the sulphate is not great, enough could be dissolved, by percolating ground waters, to account for the barytes in these sediments. Barium carbonate is more easily soluble, and interaction with a sulphate solution would result in precipitation of the barytes.

Microscopic examination of thin sections did not reveal the barytes in the Terrigal and Avoca samples, but its

character as a cementing medium could be seen in the Stanwell Park specimen.

Calcite or Siderite.—Several interesting specimens have been examined in which calcite or siderite is present as a cementing medium or as microscopic spherulites. Such specimens were collected by the author from Narrabeen Head, Wyrrabalong, Coal Cliff and Stanwell Park, and others from the Balmain Colliery (near Sydney) were kindly lent for examination by Mr. Morrison of the Mining Museum.

The Balmain specimens from depths between 919 feet and 1,200 feet showed fairly abundant carbonate cement, in many cases siderite. The rocks are sandstones and shales from above the chocolate shale horizon, chocolate shales, and other related shales. The siderite varied in quantity; in some it is subordinate in irregular patches wrapping round the grains; in others it formed up to 90% of the rock, and formed large crystallised plates enclosing quartz and felspar grains poecilitically. These resemble in structure the Fontainebleau sandstone, although the calcium carbonate may be replaced by the iron carbonate.

Of the specimens from the Balmain Colliery one (No. 3632) is particularly interesting. It is a fine grained greyish-brown rock with rounded and elongated patches of grey carbonate material. Under the microscope the rock is seen to consist of at least 50% siderite, which is present in well defined circular sections showing a radiating fibrous structure with no noticeable nucleus. These siderite spherulites are light greyish-brown in colour. They may occur individually, or several may unite to form vein-like masses. The individual spherulites vary in diameter from 0·3 mm. to 1 mm. With polarised light a four-rayed effect is obtained with complete

sections. With crossed nicols the ray effect is more defined. Invariably the spherulites are surrounded by a narrow ring of stumpy crystals or grains of carbonate, not optically continuous with the central fibres. In many cases the extreme edge of the rim is stained brown with limonite, due to oxidation. If two equal spherulites interfere the junction is a plane surface or a straight line in section. If the spherulites are unequal the contact surface is curved and concave towards the smaller spherulite. Occurrences of spherulitic siderite in sediments have been described by Spencer[22] (p. 670). The microscopic characters as observed in this rock slide correspond in detail with characters observed by Spencer.

In addition to the siderite there are rounded grains of what appear to be volcanic fragments. Some are very decomposed, but others show what is apparently trachytic fabric. In about equal number with these fragments are rounded masses of chalcedony. Sometimes the chalcedony occurs interstitially as a cement. Other grains of finely granular silica, either quartz or chalcedony, occur.

Felspar is also present in fragments up to 1 mm. across. The size is not uniform, and the shape is variable, showing rounded and straight edges. The R.I. is greater than Canada balsam (1·55). No twinning is observed. Cleavage cracks are closely developed, but no decomposition has taken place, the felspar being very fresh.

All the fragments are surrounded by a carbonate rim, which really constitutes, with chalcedony, the cement.

The felspar and volcanic fragments point to a tuffaceous origin for the rock, which could be named a siderite-tuff.

Of specimens collected by the writer, one was a fine white sandstone from Narrabeen Head. This had a

peculiar sheen, giving the rock an appearance of quartzite, and it was very tough. Under the microscope it is seen to consist of quartz grains not exceeding 0·1 mm. in diameter, set in plates of calcite. The rock is therefore a fine-grained Fontainebleau sandstone. Similar occurrences are recorded from Rock Lily, one mile north of Narrabeen[7] (p. 406), and from Stanwell Park[11] (p. 68).

Several feet below this fine sandstone is a fine dark grey shale. The microscope shows the rock to be made up of a very fine shaly groundmass which cannot be completely resolved under the microscope. Very fine quartz with indications of secondary mica can be recognised. Tiny spots of siderite are crowded through the shaly mass. Embedded in the main mass are patches of siderite. These remind one of the spherulites in specimen No. 3632, previously described, but in many points they differ. The siderite patches are neither so regular in outline nor so characteristically spherical as in the first case. There is no peripheral rim. The fibrous structure is present, but is not so regular. The fibres radiate from the centre in fan-shaped wedges, giving an irregular fluted outline to the mass (Plate VIII, 8).

Tuffaceous sandstones from Coal Cliff and Stanwell Park and a tuff interbedded with chocolate shale at Wyrrabalong have irregular patches of carbonate cement.

A tuff collected from about 30 feet above sea level at Coal Cliff was found to consist of about 80% calcite and siderite. It is rather a coarse rock consisting of pink, grey, brown and green irregular fragments. It is very tough and forms a prominent resistant band about eight inches wide in alternating sandstones and shales.

There are several irregular and rather angular fragments of quartz, averaging 0·2 mm. across, and irregular patches showing flecked grey interference colours and mica. The carbonate solutions have evidently attacked and replaced some of these fragments, since the junctions between the carbonate and the fragments are very ragged. Several volcanic fragments occur. These have been attacked and partly replaced by carbonate solutions. Fragments of chlorite are also present.

Peculiar structures are observed in some of the carbonate. These are small concretionary structures somewhat comparable with the spherulites described. Rounded or oval forms occur which have a dark nucleus, probably limonite. The rounded forms have a central nucleus, but the long oval forms have a long axis. The carbonates are deposited concentrically around these nuclei. There may be several rows of carbonate alternating with carbonate of a different texture. Radial structure is absent. Individual concretions may assume a petaloid or rosette-like structure. Other concretions are crowded together in patches.

In rocks where the calcite cement is very subordinate, it is possible that it was derived from the decomposition of felspathic material. In others where the carbonate is abundant other sources of the calcite have to be considered. David[7] (p. 407) suggests the dissolving up of ostracod values as a possible source of the calcite.

In the Coal Cliff tuff it would seem that the carbonates are essentially later than the original rock, as replacement of original material has taken place. The small concretions developed round nuclei of other material.

In the case of the perfect spherulites from Balmain we have a common carbonate rim enclosing spherulites

and other fragments. Therefore the spherulites must have developed before the final carbonate cementation of the rock.

It is probable that the material for these spherulites and for the fibrous aggregates in the Narrabeen grey shale has been concentrated as calcium carbonate in the original fine clayey material of the sediment, and this concentration has been followed by crystallisation into more or less perfect spherulitic form and metasomatic replacement by siderite. In the case of the Balmain specimen there has been further addition of carbonate which on precipitation from solution formed the cement.

NOTE.—*The Kamílaroi sediments,* so far examined by the writer, show a very interesting similarity to the Narrabeen sediments. The concentrates from Kamílaroi rocks north of the Narrabeen area are very similar to those from the northern Narrabeen rocks, and have the following minerals in common: garnet, iron oxides, pyrites, picotite, spinel, anatase, rutile, brookite, zircon (including zircon with a greenish tinge), colourless and brown apatite, tourmaline and monazite. Concentrates from the south are also similar to Narrabeen concentrates.

Thus there appears to be an interesting relationship between the two sedimentary series, but much more work needs to be done to establish the exact nature of this relationship.

(*b*) THE OCCURRENCE OF CRYSTALLISED QUARTZ IN A SANDSTONE FROM BULLI.

The sandstone outcrops near the top of the Narrabeen series on Bulli Pass.

Under the microscope it is seen to consist of clear quartz grains showing excellent enlargement, and

irresolvable rounded grains showing flecked grey interference colours. These are cemented by a fine shaly cement, some of which has given place to fine granular silica, while other patches show densely packed sericitic mica. Very little felspar is present.

It is not unusual to find enlargement of quartz grains by secondary silica, sometimes with the development of crystal outlines on the enlarged grains [12] (p. 171), [20] (p. 7, p. 9) [23] (p. 619). Enlargement has taken place in the Bulli sandstone, and in several cases the enlarged quartz grains have assumed crystal faces.

Tiny crystals of quartz have also developed. The crystals observed vary from 0·05 mm. to 0·25 mm. in length. They may occur singly or in groups showing parallel orientation. (Plate viii, 5 and 6.) Sometimes they are attached to clear original quartz grains, in which case they are usually in optical continuity. Several cases were noted of crystals growing from enlarged quartz grains. In these the crystals were not in optical continuity with the main grains, but at the contacts there was a zone of secondary quartz showing undulose extinction. In other cases the crystals appear as outgrowths from the cement (Plate VIII, 7), and apparently have no crystallographic relationship to surrounding material.

The crystals project into cavities or pore spaces in the rock. The size of the cavities varies from 0·35 mm. to less than 0·1 mm. across. Thus the openings are of capillary dimensions. Sometimes these cavities have been partly filled later by quartz enlarging adjacent grains.

This occurrence is unusual, for "where there are old nuclei which can be used the solutions deposit material

upon these; for if independent particles begin to form, these would be likely to be again dissolved and deposited upon the old larger particles"[23] (p. 619). But the growth of larger individuals at the expense of smaller

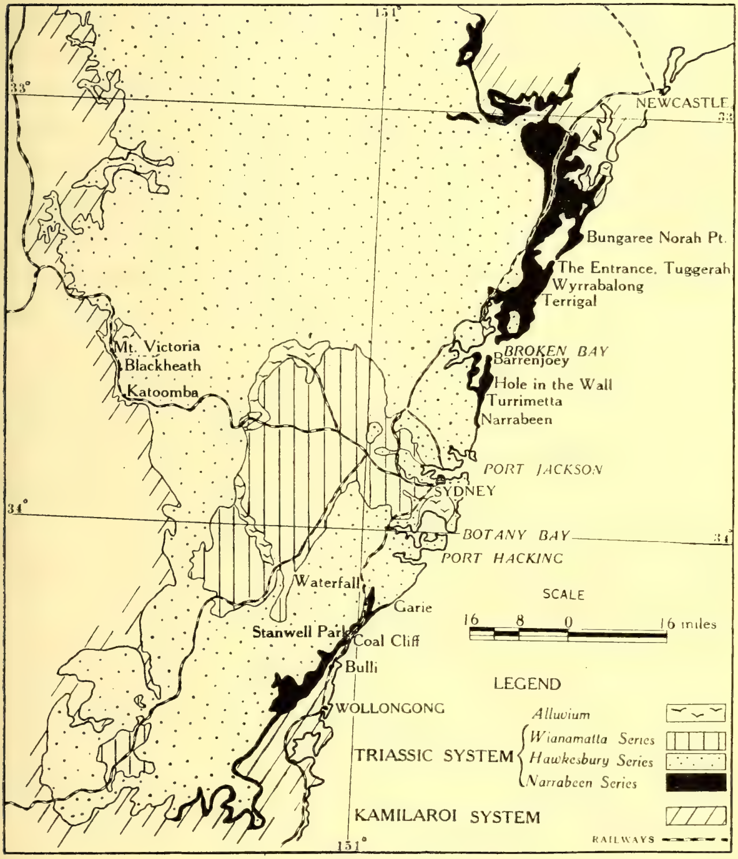

Fig. 1.—Locality Map.

Additional localities mentioned in text are: Pelican Pt., 1 mile south of Bungaree Norah Pt.; Toowoon Bay, 1 mile south of The Entrance; Wamberal, 2 miles north of Terrigal; Avoca, 1¾ miles south of Terrigal; Tudibaring, 2¾ miles south of Terrigal; Little Beach, 3¾ miles south-west of Tudibaring; Bilgola, 4 miles north of Turrimetta; Collaroy, at south end of Narrabeen beach.

ones, by the dissolving of the latter, is more rapid under conditions of high temperature and pressure[23] (p. 75).

It is suggested that these tiny crystals have been precipitated from saturated solutions of silica, very slowly circulating in capillary openings. The growth of crystals necessitates that the solution should be saturated or supersaturated at the place of growth of the crystal, and at a "moderate depth below the surface, and especially in the smaller spaces, where movement is very slow, the solutions are often saturated"[23] (p. 75). Since quartz is not "wholly insoluble in underground waters, even at ordinary temperatures and pressures"[24] (p. 319), it is possible that the crystals developed under conditions of temperature and pressure such that the tendency for re-solution was weak.

No igneous rocks are known in close proximity to this sandstone, so there appears to be no reason for postulating precipitation of the quartz under thermal conditions.

Only one other apparently similar occurrence of crystallised quartz in sandstone is known to the author. This is in the Bunter Sandstone of the English Triassic, where "in many of these beds the quartz is almost entirely in the form of minute crystals, or crystalline aggregates . . ." This rock "appears to have but little or no cementing material, and to be, to a large extent, merely felted together by the intergrowth of its constituent crystals"[20] (p. 14).

The scarcity of records of such occurrences may be partly due to the fact that comparatively little work has been done in studying thin sections of sedimentary rocks.

Summary.

(*a*) The percentage of heavy minerals in Narrabeen sediments is variable and low.

Zircon, rutile, tourmaline and picotite are constant constituents. Mauve and greenish zircons are present in the northern sediments.

Magnetite and ilmenite are commonly present.

Garnet, apatite and monazite are typical constituents of the northern sediments, and spinel and hypersthene are scarce in these.

Galena is present in sandstones from Mt. Victoria, and is derived from sulphide ore deposits in a Devonian batholith to the west.

Chalcopyrite and pyrites occur locally.

Barytes is present in several concentrates as idiomorphic individuals and has been formed *in situ* by percolating waters.

Authigenic anatase is common and may be accompanied by secondary rutile, brookite and leucoxene.

In specimens from the Balmain Colliery, Narrabeen and Coal Cliff spherulites of calcite and siderite have been observed.

No definite conclusions as regards the origin of the Narrabeen beds have been stated, although a mineralogical relationship with the older and underlying Kamílaroi System is suspected.

(*b*) A record is made of the presence of crystallised quartz in a sandstone from near the top of the Narrabeen Series at Bulli. Original quartz grains show enlargement by secondary silica with the development of crystal faces in some cases. Also new crystals up to 0·25 mm. in length have developed in capillary cavities. These may,

or may not, be in optical continuity with the quartz grains on which they have grown.

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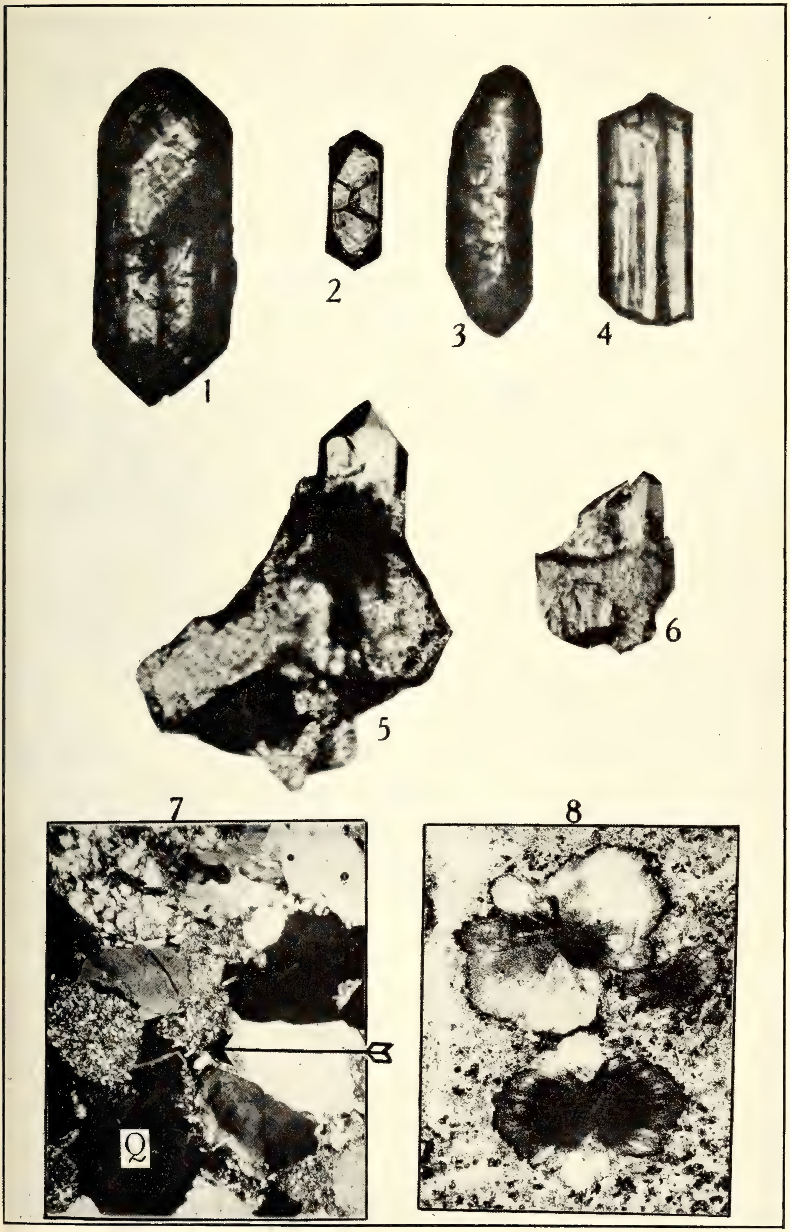
Photos by H. G. Gooch.



Photos by H. G. Gooch.

Explanation of Plates.

Plate VII.

1 and 2. Anatase (×100), Wamberal. Typical flat crystals. The dark border is due to shadows thrown on the thick broken edges.

3. Anatase (×68), Turrimetta. Bipyramidal crystal.
4. Apatite (×100), Toowoon Bay. Light brown. Note inclusion.
5. Apatite (×100), Wyrrabalong. Colourless.
6. Apatite (×100), Toowoon Bay. Brown.

7, 8 and 9. Barytes (×100), Stanwell Park. Stumpy grains showing tendency to crystal form.

10. Barytes (×100), Avoca. Cleavage plate.
11. Brookite (×100), Wyrrabalong. Showing vertical striations.
12. Brookite (×100), Mt. Victoria. Showing vertical striations.
13. Galena (×100), Mt. Victoria. Cleavage fragment.
14. Garnet (×100), Toowoon Bay. Irregular grain.
15. Garnet (×100), Terrigal. Irregular grain.
16. Monazite (×100), Terrigal. Typical rounded grain.
17. Monazite (×100), Avoca. Typical rounded grain.
18. Picotite (×100), Coal Cliff. Twinned crystal.
19. Rutile (×100), Turrimetta.
20. Rutile (×100), Toowoon Bay.
21. Tourmaline (×100), Avoca. Crystal showing trigonal symmetry.
22. Tourmaline (×100), Avoca. Worn grain.
23. Tourmaline (×100), Turrimetta.

Plate VIII.

1. Zircon (×100), Turrimetta. Showing zoning and irregular inclusions.
2. Zircon (×100), Toowoon Bay. Showing zoning and central inclusion.
3. Zircon (×100), Wamberal. Slightly worn crystal.
4. Zircon (×100), Wamberal.
5. Quartz crystal (×68), Bulli sandstone.
6. Quartz crystals, showing parallel growth from quartz grain (×100), Bulli sandstone.
7. Bulli sandstone, showing two small quartz crystals growing parallel into a microscopic cavity. A white line is drawn between the cavity and a quartz grain which is at extinction. Crossed nicols. (×50.)
8. Narrabeen grey shale, showing imperfect siderite spherulites, in very fine shale groundmass dotted with siderite grains. Polarised light. (×34.)

A NOTE ON THE OCCURRENCE OF β-CRISTOBALITE IN AUSTRALIAN OPALS.

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and D. P. Mellor, M.Sc.

(Read before the Royal Society of New South Wales, Nov. 2, 1932.)

Earlier examination of opal by the Hull-Debye powder method (Lehmann, *Z. Krist*, **59**, 455, 1923; Rinne, *Z. Krist*, **60**, 55, 1924) seemed to show that it belonged to the small class of truly amorphous solids. A photograph of common opal taken in this laboratory some time ago also showed only the broad band characteristic of amorphism. Since that time it has been reported (Levin and Ott, *J.A.C.S.*, **54**, 828, 1932) that opals show definite crystallinity and that the pattern they produce is identical with that of β (high) cristobalite. The question has therefore been taken up again and opals from various Australian sources have been examined.

In a number of instances photographs showing definite diffraction patterns have been obtained, while in other cases there appeared only a rather broad diffuse band. Table I summarises the results obtained.

The measurements (Table II) made on a film calibrated in the usual way with electrolytic copper confirm the existence of β (high) cristobalite in both common and precious opal.

TABLE I.

No. of Specimen.	Locality.	Type of Opal.	Nature of Diffraction Pattern.
1	Tintenbar, New South Wales.	Transparent precious opal.	Pattern identical with that produced by β (high) cristobalite. Broad lines.
2	Oodnadatta, South Australia.	Translucent precious opal.	Similar to 1, but with much broader lines.
3	Lismore, New South Wales.	Common opal (altered diatomaceous earth).	Similar to 1.
4	Forbes, New South Wales.	Wood opal,* opaque, pale yellow.	Similar to 1.
5	Lightning Ridge, New South Wales.	Precious (black) opal.	Single diffuse broad band.
6	Lightning Ridge, New South Wales.	Common or potch opal, dark bluish grey.	Single diffuse broad band.
7	Coober Pedy, South Australia.	Milky precious opal.	Single diffuse broad band.
8	Querétaro, Mexico.	Transparent amber coloured.	Similar to 1, but with much sharper lines.

*Silicified wood gave rise to a pattern identical with that of α quartz.

TABLE II.

Plane.	Spacing Calculated from Photograph of Specimen No. 1.	Spacing (T. W. Barth *A.J.Sc.* **23**, 350, 1932)
(111)	4·15	4·15
(220)	2·51	2·53
(222)	2·09	2·07
(133)	1·66	1·64
(224)	1·48	1·46

The broad band noted in Column 3, Table I, is located in the position of the most intense line of the β cristobalite pattern. Randall, Rooksby and Cooper (*Z. Krist*, **75**, 201, 1930) have shown that the broad band produced by vitreous and precipitated "amorphous" silica is in the position of the most intense line of the diffraction pattern of α (low) cristobalite. These authors consider that the band is due to the presence of crystallites of the order of 10^{-6}–10^{-7} cm. diameter. If this interpretation is correct then the broad band of opal is produced by crystallites of β cristobalite of the same order of magnitude. It is, of course, impossible to derive any idea of the proportion of the opal which exists in the form of β cristobalite from diffraction data.

If opals originated from hydrated silica precipitated from aqueous silicate solutions, and hence from material containing α cristobalite, then at some time opals in which β cristobalite is present, that is, all opals so far examined, must have been heated above 200–275° C., the inversion temperature range of α cristobalite. (Note: The temperature of inversion of α cristobalite to the β form is variable. See Sosman: "Properties of Silica," *A.C.S.*, Monograph Series, No. 37, 1927.) It is not clear why the size of the crystallites

should vary in opals from the different localities. It has been suggested to us by Professor W. R. Browne that in some cases (No. 1 and No. 3) where relatively sharp lines occur in the diffraction patterns, the material may have been affected by thermal effects of lava flows subsequent to the deposition of hydrated silica. Specimens No. 1 and No. 7, when heated for 6 to 8 hours at approximately 1,000° C., gave rise to just perceptibly sharper lines than the same specimens before heat treatment. Incidentally, it may be of interest to note that such drastic thermal treatment did not destroy the interference colours of precious opal. Similar heat treatment of hydrated silica which had been precipitated from sodium silicate solution and subsequently subjected to prolonged washing until free from soluble chlorides failed to show anything more than a broad band. This confirms the experience of Küstner and Remy (*Physik. Zeit.*, **24**, 25, 1923), but is contrary to the experience of Kyropoulos (*Zeit. Anorg. Chem.*, **99**, 197, 1917).

It seems possible that the growth of crystallites during heat treatment (α cristobalite in the case of precipitated silica and β cristobalite in the case of opals) depends to some extent on the presence of traces of impurities which may function through a process of solution and recrystallisation. The effect of the presence of impurities may explain the contradiction of the above experiments. In order to test this point further, some common opal whose diffraction pattern consisted of a broad band only, was ground up and heated with a small amount of chemically pure potassium chloride at approximately 1,000° for four hours. After further grinding and careful washing until free from potassium chloride, a powder photograph revealed a definite sharp diffraction pattern of β cristobalite. Thus by heating opal in the presence of a

flux, it was possible to grow the β cristobalite crystals. Professor Browne suggests that this process may occur in nature by the effect of the action of magmatic waters during lava flows.

The authors wish to thank the following: Professor W. R. Browne, for his advice on various aspects of the work; Mr. Percy Marks, who kindly supplied specimens of precious opal from all of the most important Australian fields; Mr. T. Hodge-Smith, of the Australian Museum, who supplied various specimens; and Mr. M. Whitworth, of the Mining Museum, who supplied a small specimen of Mexican opal from Querétaro.

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AN AVERAGE MOISTURE EQUILIBRIUM FOR WOOD.

By M. B. WELCH, B.Sc., A.I.C.,
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(With one text-figure.)

(Read before the Royal Society of New South Wales, Nov. 2, 1932.)

The condition of seasoning of timber is one of the most important factors in the successful utilisation of this material, and the only sound indication of the degree of seasoning is obtained by determining the moisture content of the wood. As is well known, timber loses or absorbs moisture when exposed for a sufficient period to conditions of low or high atmospheric humidity, and if the exposure is sufficiently prolonged, an equilibrium condition is attained. In practice, except in damp unventilated positions, *e.g.*, cellars, or in dry unventilated situations, *e.g.*, near boilers or steam pipes, variations in atmospheric humidity are constantly occurring, and hence the moisture content of the wood is always fluctuating above and below an average equilibrium moisture figure, and it is important to determine approximately what this figure is.

Apart from the constant fluctuation due to varying atmospheric conditions, different timbers exposed to similar conditions do not always contain the same amount of moisture,* and therefore an exact figure is

* M. B. Welch, "Experiments on Moisture in Timber," *Proc. Roy. Soc. N.S.W.*, lxiv, 337-351, 1930.

impossible; furthermore, variation may even occur in the same board.

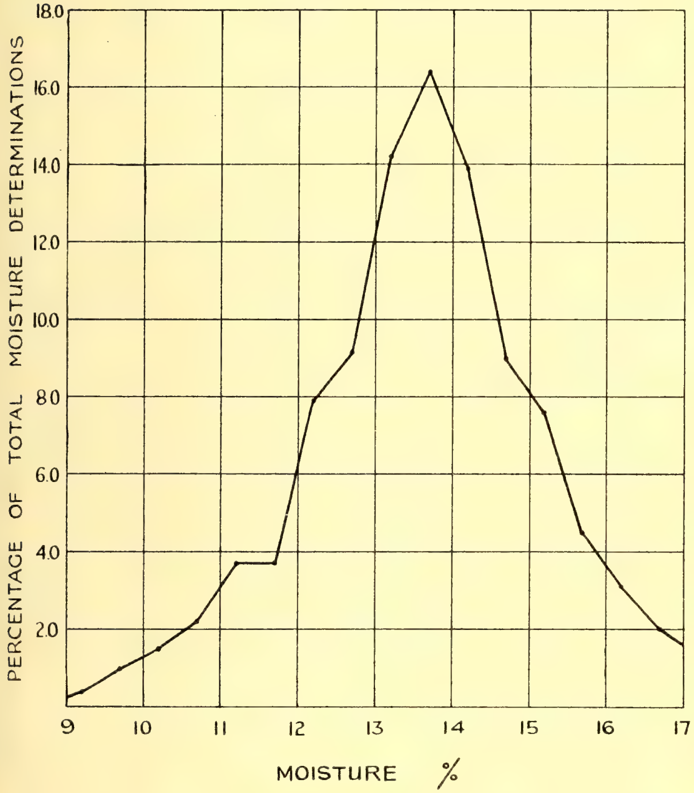
It can readily be seen therefore that it is impracticable to insist that a timber should contain a certain percentage of moisture, although this is frequently done, and rather a certain tolerance above and below an average value should be permitted.

During the past six years a large number of moisture determinations have been made on a wide range of air-seasoned timbers at the Technological Museum, and it was thought that an analysis of the figures should be of some value in indicating the approximate moisture equilibrium range. Many of the samples examined were submitted by timber suppliers or consumers, others were cut from specimens which had been used for mechanical tests. The range from 9·0 to 17·0% was divided into sixteen divisions, each representing 0·5%, and the number of moisture determinations which occurred in each division was counted, the actual limits to each division being 9·0–9·4%, 9·5–9·9%, 10·0–10·4% *et cetera*. The results were plotted in the accompanying graph (Figure 1), the abscissæ representing the percentage of moisture and the ordinates indicating the number or frequency of the moisture determinations found in each 0·5% division, expressed as a percentage of the total number of determinations, which amounted to 1,246. Results over 17% were regarded as too high for seasoned timber and were not used.

The graph shows a comparatively symmetrical probability "curve" and shows a very definite maximum frequency of 16·4% in the division corresponding to a moisture percentage of 13·5–13·9. For the divisions corresponding to 13·0–13·4 and 14·0–14·4 moisture content, the frequency percentages are 14·2 and 13·9

respectively; 62·6% of the total determinations fall between 12·5 and 14·9% moisture, 78·1% fall between 12·0 and 15·4% moisture.

FIGURE I.



If the assumption is made that the average equilibrium moisture percentage corresponds with the figure most commonly obtained, then it appears that this moisture content for the Sydney district, for the timbers examined, is in the vicinity of 13·7% (13·5–13·9%). In a previous experiment (*l.c.*) a mean of 12·7% was obtained, but the

material examined was kept indoors in a room with a northerly aspect, thus probably accounting to some degree for the lower figure. In the moisture determinations now under review there is a large preponderance of hard woods, whose equilibrium figures are often higher than those of soft woods. Again, the figure obtained from the graph would, if anything, tend to be on the high side, since there is always a possibility that some of the timbers submitted may not have quite attained a true equilibrium.

1·4% of the results are under 10% moisture, indicating that comparatively low moisture contents are occasionally obtained for air-seasoned timber in Sydney. Such figures evidently correspond to tests made during exceptionally dry periods which do not appear to occur in any particular season.

An attempt was made to dissect the moisture figures recorded for each month in order to determine whether any seasonal fluctuation could be traced. The results were inconclusive, some months showing two maximum frequencies corresponding to moisture percentages as much as 2% apart, indicating that what is a dry month in some years may be comparatively wet in other years.

THE QUANTITATIVE THEORY OF INTERACTION BETWEEN DIFFERENT SPECIES OF ANIMALS.

By V. A. BAILEY, M.A., D.Phil. (Oxon), F.Inst.P.,
Associate Professor of Physics, University of Sydney.

(Read before the Royal Society of New South Wales, Nov. 2, 1932.)

At a joint meeting of Sections A and D of the Australian and New Zealand Association for the Advancement of Science in August last, Dr. A. J. Nicholson gave a brief analysis of the factors which essentially determine the magnitude of animal populations.

Since the theory of quantity is a branch of mathematics, and since the problem of animal populations is of considerable complexity, it is necessary to apply to this problem a thorough-going mathematical analysis. Accordingly, with the biological data as postulates, a *purely deductive* theory has been developed, part of which has already been published in the *Quarterly Journal of Mathematics* (Oxford Series) for March, 1931, and was briefly outlined at the above-mentioned joint meeting.

The biological foundations supplied by Dr. Nicholson will not be again discussed here, as they are being published elsewhere. But it is of interest to give a brief summary of the mathematical theory which, in the hands of a mathematician, will serve to derive the necessary properties of animal populations. The biological notions adopted are implied in the notation defined below.

The selection of parasitic species as enemies is made because they belong to the type of predator whose properties can be most simply represented.

In the following notation an upper index refers to a particular parasite-species and a lower index to a particular host-species.

Let us denote by

ξ or η the age of an animal,

$f(\xi)$ the probability at birth that, in the absence of parasites, an animal will survive environmental causes of death till the age ξ,

$k_q(\xi)$ the probability at its birth, that a q-host, when aged ξ, will bear one new host per unit time,

$\gamma_q^p(\xi)$ the probability that a q-host of age ξ be in a condition to interact with the p-parasites.

$v_q^p(\eta)$ the effective velocity, areal or volumetric, of p-parasites of age η, in regard to their ability to find (and attack) q-hosts.

l_q^p the number of eggs laid by a p-parasite in a q-host.

$g_q^p(\xi) = \gamma_q^p(\xi) f_q(\xi)$,

$j_q^p(\eta) = v_q^p(\eta) f^p(\eta)$.

P the number of parasite-species,

Q the number of host-species.

The above functions specify the essential properties of the species.

The following functions represent unknown quantities which need to be determined:

$N(t)$ density at time t, of all the animals of a given species,

$M^p_q(t)$ density at time t of those q-hosts which are in a condition to interact with p-parasites,

$W^p_q(t)$ effective velocity at time t of the whole of the p-parasites in regard to their finding q-hosts,

$B(t)$ birth rate at time t of animals of a given species per unit area,

$A(t, \xi)$ age-distribution function at time t.

By means of arguments similar to those used in the *Quarterly Journal of Mathematics*, the following system of fundamental equations is deduced:

$$B_q(t) = \int_0^\infty B_q(t-\xi)k_q(\xi)\ \exp.\{\int_0^\xi -\Sigma^p W^p_q(t-\xi+x)\gamma^p_q(x)dx\}d\xi \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

$$M^p_q(t) = \int_0^\infty B_q(t-\xi)g^p_q(\xi)\ \exp.\{\int_0^\xi -\Sigma^p W^p_q(t-\xi+x)\gamma^p_q(x)dx\}d\xi \qquad \ldots\ldots\ldots\ldots\ldots(2)$$

$$W^p_q(t = \int_0^\infty B^p(t-\eta)j^p_q(\eta)d\eta \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$B^p(t) = \Sigma_q l^p_q M^p_q(t) W^p_q(t) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

This system has as many equations as unknown quantities.

When the values of B^p and B_q are known for all moments preceding $t = 0$ the functions $B^p(t)$ and $B_q(t)$ are determined by this system of equations for any later time t. We can then derive the densities $N^p(t)$, $N_q(t)$ and the age-distributions $A^p(t, \xi)$, $A_q(t, \eta)$.

A steady state is conceivable in which the various quantities B^p, B_q, M^p_q, W^p_q do not change with time. In such a situation if b^p, b_q, m^p_q, w^p_q represent their respective

values they are determined by the following system of equations :

$$1=\int_0^\infty k_q(\xi)\ \exp.\{-\Sigma^p w_q^p\int_0^\xi \gamma_q^p(x)dx\}d\xi \quad \ldots\ldots\ldots\ldots\ldots (5)$$

$$m_q^p=b_q\int_0^\infty g_q^p(\xi)\ \exp.\{-\Sigma^p w_q^p\int_0^\xi \gamma_q^p(x)dx\}d\xi \ldots\ldots\ldots\ldots\ldots (6)$$

$$w_q^p=b^p\int_0^\infty j_q^p(\eta)d\eta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

$$b^p=\Sigma_q l_q^p m_q^p w_q^p \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

When the number Q of host-species exceeds the number P of parasite-species the combination of (5) with (7) yields more than P equations in the P unknowns. Hence a steady state is not then possible.

When P is greater than Q the possibility of a steady state depends on the properties of the interacting species.

Thus, as Dr. Nicholson has discovered (and I have verified), when Q = 1 and P > Q the steady state is sometimes possible when the different parasite-species attack the host-species at different parts of its life-cycle.

On the other hand, when all the functions $\gamma_q^p(\xi)$ are similar, *i.e.*, of the form $\gamma_q^p(\xi)=c_q^p\gamma(\xi)$ where the c_q^p's are different constants, the steady state in general cannot exist.

When P is equal to Q then, subject to the densities being positive, the steady state in general is possible, even when the $\gamma_q^p(\xi)$'s are similar.

The discussion of the solutions of the system (1)–(4) is difficult, but a considerable reduction of the difficulties occurs when the discussion is restricted to those host-

species whose individuals have a probability of interaction which is independent of their ages, *i.e.*, for which $\gamma^p_q(\xi)=c^p_q$, a constant. This requires also that $P=Q$.

On introducing the functions

$$Z^q_p(t)=c^p_q\int_0^t W^q_p(\tau)d\tau$$

$$X_q(t)=B_q(t)e^{\Sigma^p Z^p_q(t)}$$

the fundamental equations (1) to (4) become respectively

$$X_q(t)=\int_0^{T_q} X_q(t-\xi)k_q(\xi)d\xi \quad\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

$$M^p_q(t)e^{\Sigma^p Z^p_q(t)}=\int_0^{T_q} X_q(t-\xi)g^p_q(\xi)d\xi \quad\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

$$Z^{p\prime}_q(t)=c^p_q\int_0^{T^p} B^p(t-\eta)j^p_q(\eta)d\eta \quad\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

$$B^p(t)=\Sigma_q(l^p_q/c^p_q M^p_q(t)Z^{p\prime}_q(t) \ldots\ldots\ldots\ldots\ldots\ldots(12)$$

From these a system of equations in the B^p's alone can be derived. As $t\to\infty$ this system tends to the following form

$$B^p(t)=\Sigma_q[(c_q l^p_q m^p_q/c^p_q b_q)\int_0^{T^p} B^p(t-\eta)i^p_q(\eta)d\eta \;\times$$

$$e^{-\Sigma^s}\int_0^t dt\int_0^{T_s}\beta^s(t-\theta)i^s_q(\theta)d\theta] \quad\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

where $\beta^p(t)=B^p(t)-b^p$.

By means of (13) we can in particular study the behaviour of the population *near* the steady state. The principal conclusion so far derived is as follows:

When one host-species interacts with one parasite-species then (to a first approximation) their densities

with the lapse of time *oscillate about their steady values with increasing violence.*

The details of the general theory and its extension to include hyperparasites are being published elsewhere.

On account of its relative simplicity we may also consider Dr. Nicholson's special case of two species whose life-cycles are concurrent and whose interaction takes place non-continuously as described in the publication in the *Quarterly Journal of Mathematics* (*loc. cit.*, pp. 68, 69 and 75).

Let us denote by

F the power of increase of the host-species per generation,

$N_1(t)$ the host-density at the end of the $(t-1)^{th}$ generation,

$N(t)$ the parasite-density at the end of the t^{th} generation,

a the average gross area traversed by a parasite individual during its search.

The fundamental equations are as follows:

$$N_1(t+1) = FN_1(t)e^{-aN(t)} \quad \text{(14)}$$

$$N(t+1) = FN_1(t) - N_1(t+1) \quad \text{(15)}$$

The steady densities n_1 and n are then given by these equations:

$$1 = Fe^{-an},$$

$$n = n_1(F-1).$$

To study the behaviour near the steady state we set

$$N_1(t) = n_1+\nu_1(t), \quad N(t) = n+\nu(t),$$

substitute in (14) and (15), and retain only the terms of the first order of smallness.

This yields:

$$\nu_1(t+1) = \nu_1(t) - L(F)\nu(t)$$

and

$$\nu(t+1) = F\nu_1(t) - \nu_1(t+1)$$

where

$$L(F) \equiv \frac{\log F}{F-1}$$

Eliminating $\nu(t)$ between these two equations leads to this difference-equation:

$$\nu_1(t+2) - 2b\nu_1(t+1) + c^2\nu_1(t) = 0 \quad \ldots\ldots\ldots\ldots\ldots (16)$$

where $b = \frac{1}{2}\{1 + L(F)\}$, $c = \sqrt{L(F^{-1})}$.

From its definition $F > 1$, so $b < 1$ and $c^2 > 1$. Therefore the general primitive of (16) is

$$\nu_1(t) = Ac^t \sin(\lambda t + B) \quad \ldots\ldots\ldots\ldots\ldots\ldots (17)$$

where A and B are arbitrary constants, $c = +\sqrt{L(F^{-1})}$ and $\lambda = \cos^{-1}\left(\frac{1 + L(F)}{2\sqrt{L(F^{-1})}}\right)$.

It then follows that $\nu(t)$ is given by a similar expression.

Thus the densities oscillate about the steady values with amplitudes which increase with time.

It is noteworthy that formula (17) gives numerical results with the values $F = 2$ and 4 which are in close agreement with results obtained previously by Dr. Nicholson by arithmetical reasoning.

It can also be shown that even away from the steady values the densities must oscillate perpetually about them.

RELATION OF THE TERTIARY ALKALINE ROCKS OF EASTERN AUSTRALIA TO LATE TERTIARY TECTONIC LINES.

By C. A. SUSSMILCH, F.G.S.

(With two text-figures.)

(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

The position of the various known occurrences of alkaline igneous rocks of Tertiary age in New South Wales is shown on the accompanying map (Fig. 1). It will be seen from this diagram that these occurrences are, with one exception, arranged in two parallel lines: (*a*) the western line, and (*b*) the eastern line, each having an approximate meridional trend, the two lines being situated along the western and eastern margins respectively of the main tableland belt of New South Wales. The exception is the group of laccolites occurring near the town of Rylstone, and it will be shown later that this occurs along an east-west line of fracture.

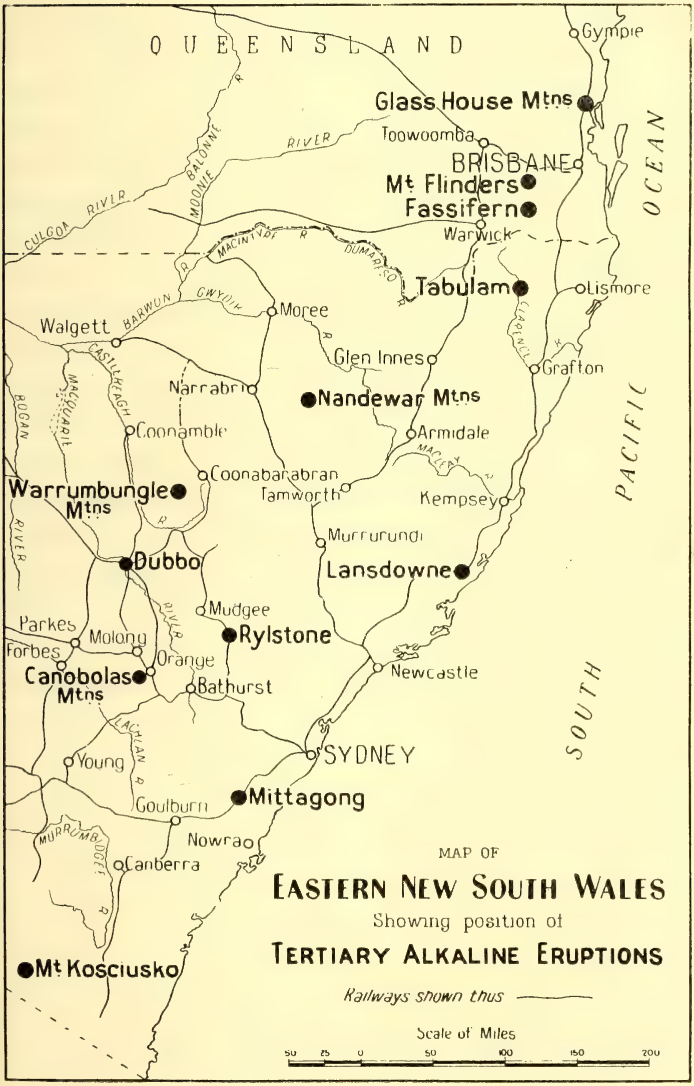
The object of this paper is to show that these alkaline rocks are definitely associated with some of the main tectonic lines of the great Kosciusko uplift which affected eastern Australia at or near the close of the Pliocene period, but that their extrusion and intrusion appears to have preceded the actual uplift.

(a) The Western Line.

The known occurrences along the western line are as follows:

1. Mt. Kosciusko—a phonolite dyke.
2. The Canobolas Mountains—a group of extinct volcanoes.

3. The Dubbo Trachyte flows and necks.
4. The Warrumbungle Mountains—a group of extinct volcanoes.



5. The Nandewar Mountains—a group of extinct volcanoes.

1. *Mt. Kosciusko.*—The occurrence here of a phonolite dyke has been recorded by Sir T. W. E. David[1]; it is situated close to the great fault scarp which lies along the western margin of the Mt. Kosciusko tableland. The only evidence of the age of this dyke is that it is Post-Ordovician. There is therefore no proof of it having the same geological age as the other occurrences along this western line, but it is usually, on account of its chemical composition, included with the other alkaline rocks of eastern Australia.

2. *The Canobolas Mountains.*—This is a group of extinct volcanoes situated close to the town of Orange on the Central tableland; it will be convenient to refer to this part as the Orange tableland. It has an altitude of about 3,100′. The geology of the Canobolas Mountains has been described by Sussmilch and Jenson,[2] who have shown them to consist mainly of comendites, trachytes and andesites with their associated tuffs, the series as a whole being strongly alkaline. The more important volcanic cones are ranged along a definite north-south line, and this line is adjacent to the western margin of the tableland, where it breaks away somewhat suddenly to the western plains. The geomorphology of this region has not previously been described in detail; its essential features are shown in the sketch in Fig. 2. It will be seen from this section that immediately to the

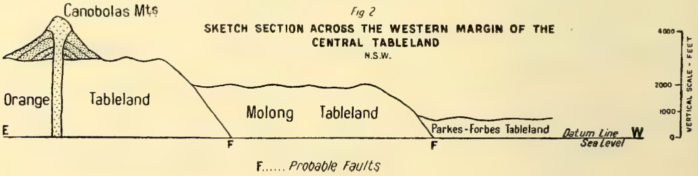


Fig 2
SKETCH SECTION ACROSS THE WESTERN MARGIN OF THE CENTRAL TABLELAND
N.S.W.

F...... *Probable Faults*

west of the Canobolas Mountains the Orange tableland breaks away to the west in a series of steps and treads, the first step giving a drop of about 1,000′ to the Molong tableland. This latter tableland has an elevation of about 2,100′, its surface topography is markedly similar to that of the adjoining higher Orange tableland, and its underlying geological structure is the same, that is, it consists of folded Silurian and Devonian strata and their associated plutonic intrusions. There is nothing in the geological structure to suggest that the difference in elevation between the two tablelands has resulted from differential erosion. The Molong tableland has a width in an east-west direction of about 30 miles and extends for many miles in a north-south direction. At its western margin it breaks away suddenly with a drop of about 1,100′ to the Parkes-Forbes tableland, the latter having an altitude of about 1,000′. The scarp which separates the Orange tableland from the Molong tableland, and also the one which separates the latter from the Parkes-Forbes tableland are from the physiographical evidence considered to be tectonic scarps with an approximately meridional trend and with a throw in each case of about 1,000′, but in the absence of detailed geological maps it is impossible to determine whether these scarps are due to faulting or to monoclinal folding; they are considered by the writer to have been developed as a result of differential movement during the uplift which produced the present tablelands (Kosciusko epoch). It will be seen from the above description that the Canobolas Mountains occur adjacent to and on the upthrow side of a tectonic scarp.

3. *The Dubbo Trachytes.*—Adjacent to the town of Dubbo, some considerable distance to the north of Orange, there occur some flows and plugs of alkaline trachytes[15]

about which very little information is available. They occur on a tableland at an altitude of about 1,000′ above sea level, possibly a northern extension of the Parkes-Forbes level.

4. *The Warrumbungle Mountains.*—This is a group of extinct volcanoes situated near the town of Coonabarabran some 70 miles to the north of the Canobolas Mountains. They have been described in detail by Dr. H. I. Jensen,[3] and his description shows them to be similar in every way to the Canobolas Mountains. These volcanoes lie on a tableland at an altitude of about 2,000′, which, from Dr. Jensen's description, appears to be similar in its physiographical features to that of the Molong tableland, but here the surface rocks consist mainly of Jurassic sandstones. This tableland would appear to be a northerly continuation of the Molong tableland. Immediately to the west of the Warrumbungle Mountains there is a steep drop from the 2,000′ level to a lower tableland with an altitude of about 1,000′. This latter would correspond to the Parkes-Forbes level further to the south.

5. *The Nandewar Mountains.*—This is a group of extinct volcanic cones lying between the towns of Narrabri, Barraba and Bingara, and about 50 miles to the north of the Warrumbungle Mountains. These volcanoes have also been described by Dr. H. I. Jensen,[4] who shows the lavas and tuffs to be identical with those of the Canobolas and Warrumbungle Mountains. The geomorphology of the western margin of the New England tableland has not previously been described, but it appears to be similar in all its main features to that already described for the western margin of the Orange tableland. The New England tableland proper has an altitude of about 3,000′. To the west of Glen

Innes there is a drop of 1,000′ on to the Barraba-Inverell tableland and immediately to the west of Barraba there is a further drop of about 600′ on to the tableland on which the Nandewar Mountains stand, this lower tableland having, according to Jensen, an altitude of about 1,400′. It will be convenient to call this tableland the Nandewar tableland. In his description of this region Jensen refers to the existence of an important fault running immediately to the east of the Nandewar Mountains, his determination being based on the geological evidence. This supports the physiographical evidence of the 1,400′ Nandewar tableland being separated from the 2,000′ Barraba-Inverell tableland by a line of faulting. Dr. Jensen has informed the writer verbally that this fault has displaced some of the Nandewar alkaline lava flows, showing that the faulting took place after the vulcanicity.

Jensen states further that "at various points between the Warrumbungle and Nandewar Mountains, along the Narrabri-Dubbo railway line, small eruptive cones and plugs of alkaline rocks occur such as at Scabby Rock in the Pillaga Scrub."

From the above descriptions it will be seen that the main tableland of New South Wales on its western side breaks off in a series of steps along a series of north-south tectonic lines which are either lines of faulting or monoclinal folding (or both) and that the various centres of volcanic activity referred to are quite closely related to these tectonic features.

(b) The Eastern Line.

The known occurrences along the eastern line of alkaline eruptions are given in the following table, in which are also included some occurrences in south-

eastern Queensland which are situated on a continuation of this line:

1. The Mittagong District—laccolites and lava cones.
2. The Lansdowne District—group of trachytic plugs.
3. The Clarence River District—trachyte lava flows.
4. The Fassifern District, south-eastern Queensland—trachyte lava flows and lava cones.
5. The Mt. Flinders Range, south-eastern Queensland—a group of extinct volcanoes.
6. The Glass House Mountains, south-eastern Queensland—a group of extinct volcanoes.

1. *The Mittagong District.*—This district consists of a tableland about 2,100′ in altitude and on its surface is a series of laccolites and lava cones extending along a south-east north-west line from "The Gib" to Mt. Jellore. These occurrences have been described by Mawson and Taylor,(5) who show them to consist of alkaline trachytes and allied rocks. This line of alkaline rocks is situated close to the well-known tectonic scarp which separates the Mittagong tableland from the low-lying Sydney senkungsfeld which lies immediately to the north. That this scarp was a tectonic one was first suggested by E. C. Andrews,(6) and was later described by Harper(7) as a monoclinal fold, the latter suggesting that it is continuous with the well-known north-south monoclinal fold which marks the eastern margin of the Blue Mountain tableland and which here swings round the southern margin of the Sydney senkungsfeld.

2. *The Lansdowne District.*—There occurs here on the eastern margin of the Comboyne tableland a group of trachytic plugs with a general north-south trend. No geological description of this region has yet been

published, but the author has had access to an unpublished paper by C. T. Grout-Smith, B.Sc., on the geology of this area. His description shows quite conclusively that the eastern margin of the Comboyne tableland is a scarp produced by monoclinal folding accompanied by some faulting and that the trachytic plugs are situated along this scarp. The Comboyne tableland itself has an altitude of 2,200′, while the coastal plain which lies immediately to the east of it has an altitude of only about 400′.

3. *The Clarence River Area.*—Alkaline trachytes have been reported as occurring at several places in this district, but nothing has yet been published about them. Mr. M. Morrison informs me that trachytes occur at Tabulum where the road from Lismore to Tenterfield crosses the scarp which here marks the eastern edge of the New England tableland, and that these rocks extend southwards to within 30 or 40 miles of Nymboida. This scarp is considered by E. C. Andrews[6] to be a tectonic scarp separating the New England tableland from the low lying Clarence River senkungsfeld.

4. *The Fassifern District.*—This occurs in south-eastern Queensland just across the New South Wales border and is a region of marked block faulting. Here trachyte lava flows and tuffs occur both on the upthrow and downthrow side of the Main Range fault. On the downthrow side of the fault there are also a number of isolated trachyte lava cones such as Mt. Greville, Mt. Edward *et cetera*. The igneous rocks of this region have been described and mapped by H. C. Richards,[8] while the physiography has been described recently by the writer.[10]

5. *The Mt. Flinders Range.*—This lies adjacent to the town of Ipswich and consists of a chain of extinct

volcanoes with a north-south trend lying adjacent to and on the upthrow side of the tectonic scarp which separates the Mt. Flinders horst from the Fassifern senkungsfeld. The geology of this region has been described in detail by H. I. Jensen,[9] while the physiography has been described by the writer.[10]

6. *The Glass House Mountains.*—This is a group of extinct volcanoes situated on the coastal plain of Queensland immediately to the north of the town of Caboolture. They have been described by H. I. Jensen,[11] who shows them to be ranged along two well marked north-south lines close to the foot of the eastern scarp of the D'Aguilar horst; one of the cones, however, Mt. Beerwah, is situated on the horst itself just at the top of the scarp. The physiographic features of this region suggest that the scarp is a fault scarp and Jensen's description[12] of the geology of the region immediately to the north shows that in that direction this fault merges into a monoclinal fold.

(c) The Laccolites of the Rylstone District.

These are situated a few miles to the north of the town of Rylstone near the northern margin of the Blue Mountain tableland. The laccolites consist of alkaline rocks (tinguaites) which have been shown by J. E. Carne[13] to intrude the Triassic rocks of that region. The geological evidence, therefore, only shows their age to be Post-Triassic, but on account of their close chemical resemblance to the tertiary alkaline rocks they are usually considered to be of the same age. These laccolites lie along an east-west tectonic line which separates the Blue Mountain tableland, whose altitude here is about 3,000′, from the low-lying Goulburn River tableland which lies immediately to the north and which

has an altitude of only about 1,450′. The tectonic line separating these two regions is partly due to monoclinal folding and partly to faulting. The details of the physiography of this region will be described by the author in a later paper. The Goulburn River tableland forms part of a relatively low-lying region which stretches right across the main tableland belt of New South Wales and separates the northern and central tablelands from one another.

From the above facts it will be seen that all the known occurrences of alkaline rocks of Tertiary age in New South Wales and south-eastern Queensland are situated along important tectonic lines associated with that great belt of tablelands which occurs in this region parallel to and adjacent to the coast line. The epeirogenic uplift which produced these tablelands was a differential one and was accompanied by the formation of well-marked lines of normal faulting and monoclinal folding, the more important of which parallel the main axis of uplift. This upward movement is generally considered to have taken place at the close of Tertiary time (Kosciusko epoch).

Such evidence as is available indicates that the outpouring and intrusion of these alkaline rocks occurred prior to the actual uplift of the tableland, but their very general situation with an orientation parallel to and in some cases actually coincident with major Kosciusko tectonic lines implies some causal relation between the two. This suggests that lines of tensional weakness had already developed in the earth's crust before the uplift and displacement began and that these lines of potential faulting were favourable to the intrusion and extrusion of the alkaline rocks. There is also the further inference that the vulcanism must have

closely preceded the uplift and accompanying faulting and that its geological age, therefore, canot be earlier than the Late Pliocene, as has previously been suggested by the writer from purely physiographical evidence.[14]

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A POSSIBLE CORRELATION OF CERTAIN PRE-CAMBRIAN GRANITES OF AUSTRALIA AND SOME DEDUCTIONS THEREFROM.

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(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

I. Introduction.

The pre-Cambrian rocks in Australia outcrop over a very extensive area, and a considerable amount of research has been published on them, but much yet remains to be done. Correlations, even within the limits of a single State, are somewhat difficult, partly owing to the absence of fossils, and to the lack of continuous outcrops, but partly also owing to incomplete detailed field-knowledge and laboratory investigation. Attempts have been made both at intra-State and at inter-State correlation by various geologists.[1–6] These all naturally have in them some element of speculation, but they are of considerable value if only for the purpose of stimulating research in regard to the problems with which they deal.

It has been pointed out by American authorities that since plutonic rocks form such an important part of the pre-Cambrian formations correlations should include consideration of these as well as of the sedimentary rocks, and in Australia attempts have been made not merely to divide up the pre-Cambrian rocks of sedimentary origin on a stratigraphical basis, but also to distinguish epochs of igneous intrusion. It would seem that at least two such epochs can be more or less clearly recognized

in a number of the States, and the present paper is concerned with setting forth some of the evidence for these and with considering some of their implications.

II. Distribution and Stratigraphical Correlation of the Intrusions.

Western Australia.

In W.A. there are strata belonging to Archæozoic and to Lower and Upper Proterozoic time, represented chiefly by the Yilgarn, Mosquito and Nullagine Series respectively. These are separated by unconformities, and apparently associated with the diastrophic events there were injections of igneous magma both acid and basic. Of the earliest of these the exact intrusion-epoch is a matter of doubt; it may have been at or just after the close of the Yilgarn sedimentation. The rocks are gneisses, often garnetiferous. In the earlier reports of the Geological Survey these older igneous gneisses have not been separated from their associated schists of sedimentary origin. A difficulty in regard to separating the earlier from some of the later granitic intrusions arises from the fact that these latter are themselves sometimes locally gneissic. The later intrusions transgress the Mosquito Series, but are not found cutting the Nullagine Series, so their advent is placed at the close of Mosquito time, when folding of the sediments took place. A number of different types of these late-Mosquito granites have been recognised, but they are all apparently related. In particular sodic types are found, with which are associated certain ore-deposits. The late-Mosquito intrusions were on a vaster scale than anything before or since their time in Australia. In the western part of the State, south of lat. 26° S., they range over three degrees of latitude and three degrees of longitude, while in the North-West Division in the

Ashburton and Pilbara Goldfields they are widely distributed.

In the Kimberley area pre-Cambrian rocks are found in the shape of more or less highly metamorphosed sedimentary strata with "metapyrigen gneisses"; these are injected by granites overlain by a series which has been correlated with the Nullagine Series. In this area, then, there are apparently representatives of both the Archæozoic and the Proterozoic Series and of the older and newer igneous intrusions.

The older granite-gneisses, as well as the newer granites, have their equivalents in the eastern part of the State about lat. 26° in the Warburton and other ranges.

Northern Territory.

The pre-Cambrian rocks of the Kimberley area continue eastwards into the Northern Territory, where the existence of two series of metamorphosed rocks, an older and a newer, has been proved. Since these are overlain by lavas, *etc.*, belonging to the Nullagine Series of W.A., it is natural to correlate the older or Bynoe Harbour schistose series with the Yilgarn Series and the overlying or Pine Creek Series with the Mosquito Series. Among the Bynoe Harbour rocks augen gneisses and hornblende-schists are found on the north, in the Pine Creek district and Arnhem Land, and farther south in the Tanami Goldfield. The newer series are intersected by unstressed granites, regarded as pre-Cambrian, which are therefore to be reasonably correlated with the late-Mosquito granites.

In the Macdonnell and Hart's Ranges(7) the older granite-gneisses appear in association with schistose rocks, while what would appear to be the equivalents

of the late-Mosquito granites form the newer granites of the same region. These are characterised by a generally massive structure and by the occurrence of abundant pegmatite dykes.

South Australia.

The pre-Cambrian rocks in the east of W.A. appear in the north-west of S.A., in the Tomkinson, Mann and Petermann Ranges. In the Musgrave Ranges and to the south-east of them there are granitic gneisses intrusive into schists, while a younger, but still pre-Cambrian, granite is characteristic of the Everard Ranges of the south.

In his recently published geological map of the Commonwealth Sir Edgeworth David marks as Proterozoic all the granites of Eyre's Peninsula, with those around Lake Gairdner and along and south of the Transcontinental Railway. In southern Eyre's Peninsula the primary granite-gneisses of the Flinders Series are intrusive into the Hutchison schists, and the later Warrow sedimentary series is invaded by the unstressed granites of the Dutton Series. The age of the Dutton granites is not certain, but the other three are pre-Cambrian. In the neighbourhood of Moonta there is a folded gneissic granite, and another, the Arthurton granite, which has been less severely stressed, and which is considered to be later than the gneiss, though still pre-Cambrian.

The pre-Cambrian rocks underlying the Upper Proterozoic Adelaide Series in the region about Adelaide have not been stratigraphically divided. Underlying the Adelaide Series there may be representatives of more than one period of sedimentation, and in any case the most altered schistose rocks may well be of Archæozoic age. Among these are granitic augen gneisses of

ancient aspect, but in addition the rocks are traversed by a later series of intrusives belonging to what Benson has designated the Houghton magma. The rocks of the Houghton magma type are not confined to the country about Adelaide, for the pre-Cambrian rocks of Yorke's Peninsula are intersected by pegmatitic granites containing ilmenite, and comagmatic types with pegmatites rich in ilmenite occur at Mount Painter in the Flinders Range, and especially in the north-east at Boolcamata and Olary near the New South Wales border, where they occupy a very large area. These granites invade schistose rocks which are the equivalents of the Willyama Series of the Barrier Ranges, N.S.W., and are, as there, directly overlain by the tillites of the Torrowangee or Adelaide Series. Older igneous gneisses are also found here, but not abundantly. Mawson considered the Houghton magma rocks to be probably Archæozoic, but Benson preferred to regard them as Algonkian.

New South Wales.

In the Barrier Ranges the Willyama Series of highly schistose rocks has been proved to be pre-Cambrian, and is regarded as Archæozoic. The series is injected by at least two distinct groups of intrusions, an older series of primary gneisses, acid and basic, and a newer and on the whole massive series of granites, with which may possibly be grouped a series of pegmatites and greisens. The newer or Mundi Mundi granites are quite different from the older gneisses, but chemically and mineralogically resemble very closely certain phases of the Olary granite, and there can be little doubt that they are comagmatic and contemporaneous. In a recent paper[8] I put forward reasons for the view that the older igneous series mark the folding of the Willyama

Series at the close of Archæozoic time, and that the Mundi Mundi granites are derived from a magma injected in connexion with a diastrophism corresponding with that of late-Mosquito time in W.A.

Queensland.

In Queensland no equivalents of the Nullagine or Adelaide Series have been recognised, and actually it is only in the Cloncurry-Camooweal region that there is definite evidence of the pre-Cambrian age of the schistose and gneissic rocks, where they are unconformably overlain by fossiliferous Cambrian beds. There appear to be in this region an older and a younger pre-Cambrian series corresponding to the Yilgarn and Mosquito Series of W.A. respectively, and the same is true of the Normanby Goldfield, and perhaps of Facing Island. These series are distinguished by differences both in the degree of metamorphism and in the prevailing strike-directions. There appear to be representatives only of the older series at Pascoe River, the Hamilton and Coen Goldfields, the Cape and Etheridge Goldfields, Dunk Island and elsewhere, and of the younger series alone at the Gilbert and Woolgar Goldfields and Charters Towers.

In studying the older series some of the investigators have evidently been disinclined to differentiate between schists and gneisses of sedimentary and those of igneous origin; nevertheless it would seem that orthogneisses are actually present, as at Croydon, Cloncurry, Chillagoe, Einasleigh and elsewhere. Whether these are Archæozoic or Proterozoic is doubtful. In view of their very intimate association with the schists, which recalls that of the W.A. and Broken Hill older gneisses, it may perhaps be permissible tentatively to suggest that these Queensland

gneisses belong to the diastrophic epoch at the close of the Archæozoic. There are younger granites associated with some of the metamorphosed areas, but no field-evidence as to their age is forthcoming.

Victoria.

In western Victoria are schistose rocks regarded as pre-Cambrian, with granites, coarsely foliated gneisses and pegmatite veins. Whether these intrusions belong to the older or newer pre-Cambrian series is uncertain.

Tasmania.

There is an entire absence of acid igneous intrusions from the Tasmanian pre-Cambrian series of the west and north coasts, but pebbles of augen gneiss in the Proterozoic schistose conglomerate of Goat Island suggest the existence in some places of buried Archæozoic igneous rocks. Newer pre-Cambrian intrusions are missing.

Summary.

There are, therefore, reasonable grounds, admittedly not conclusive in every case, for recognising two pre-Cambrian epochs of widespread plutonic intrusion in Australia, one at the close of Archæozoic and the other about the middle of Proterozoic time, coinciding roughly with the diastrophic epochs which closed the Archæozoic and Lower Proterozoic periods of sedimentation. Though the main intrusions were, broadly speaking, granitic, they were generally accompanied by injections of more acid and more basic magma.

III. Petrological Correlations.

It is probably more than a coincidence that certain of the intrusions thus correlated on stratigraphical

grounds exhibit certain common petrological peculiarities, this term being used to include characteristics of intrusive habit, internal structures and mineralogy.

The Earlier Intrusions.

Apart from the presence of accompanying or preceding charnockitic intrusions in some places, as in the Warburton and Fraser Ranges in W.A., and in southern Eyre's Peninsula in S.A., the older or late-Archæozoic intrusions show no outstanding mineralogical peculiarities.

They are all, acid and basic alike, fairly representative calcic types. Certainly some phases of the granites are garnetiferous, but otherwise they are normally granitic on the whole. A gneissic structure is invariably shown, which is, at least in some instances, primary. The intimate penetration of the associated schists by stromatolithic and *lit-par-lit* injection is also common if not universal, but, as stated above, the presence of directive structures does not constitute an infallible guide as to age.

In habit and internal structures they all show signs of synchronous injection, and they are evidently closely connected in time with the folding and metamorphism of the sedimentary series which they invade.

The Later Intrusions.

In the mineralogy of the later pre-Cambrian intrusions certain common characteristics are evident which are of some significance. The significant minerals are in general such as are produced during the last stages of crystallisation, often appearing in the pegmatites, the mineralogy of the normal rocks generally showing no peculiarities.

In W.A. there are associated with the late-Mosquito granites, often in quartzose and albitic pegmatites, tinstone, molybdenite, wolfram, tantalite, rutile and minerals containing the rarer elements, like spodumene and amblygonite, beryl, monazite, and various uranium minerals. In addition there are ores of gold, copper and lead. Most of the auriferous deposits, with the possible exception of those of the Central Goldfields, are also connected with the late-Mosquito granites.

In the northern part of the Northern Territory in association with the later pre-Cambrian granites have been found ores of gold, copper, tin, tungsten, tantalum, molybdenum and bismuth, in addition to beryl and monazite, while from the Macdonnell and Hart's Ranges, and elsewhere in Central Australia, gold, lead, copper and bismuth ores have been reported, as well as ilmenite, rutile and beryl.

For South Australia the Houghton magma has been described as being characterised by richness in titania and to a less extent in soda. The titania is present generally in ilmenite, sphene and rutile. Ilmenite is also characteristic of the pegmatites of Yorke's Peninsula. At Normanville the rutile pegmatites also contain monazite, and at Olary and Mt. Painter radioactive ilmenite and other radioactive minerals are found in pegmatitic rocks.

Beryl has been reported from the granites of many widely separated localities, as, for example, Boolcamata, Mt. Painter, Murray Bridge-Monarto, Williamstown and Yorke's Peninsula. Mention should also be made of the copper ores of Wallaroo and Moonta associated with the pre-Cambrian Arthurton granite. Molybdenite has been reported from Wallaroo and Moonta and wolfram from

near Yankalilla, but the associations of these have not been recorded.

In the Barrier Ranges of N.S.W. tin and wolfram are associated with the greisens and pegmatites at Euriowie, but the geological age of these pegmatites is uncertain. Amblygonite has also been found at Euriowie. Rutile has been recorded from Broken Hill, without, however, any mention of its associations. Mr. E. J. Kenny, of the N.S.W. Geological Survey, informs me that ilmenite in coarse crystals occurs as segregations in masses of sillimanite at Thackaringa, possibly introduced from the magma of the Mundi Mundi granite which outcrops close by. Beryl is abundant at Thackaringa in one of the coarse pegmatites closely related to the Mundi Mundi granites, and Mr. Kenny informs me that it has been found by Mr. Mawby in similar rocks 4 miles N.W. of Broken Hill. Mr. Kenny has also called my attention to the association of veins of apatite in places with the Mundi Mundi granites, a circumstance which immediately recalls similar occurrences in South Australia.

It is perhaps pertinent at this point to discuss the age of the mineralisation in the Barrier Ranges of N.S.W. which was responsible for the silver-lead, zinc and copper ores. This has generally been assigned to a late stage in the epoch of intrusion of the older gneisses. But the mineralizing solutions which produced the Broken Hill lode and other lodes were introduced along longitudinal shear-zones through Willyama schists, and have replaced not merely schists but pegmatites which are themselves unstressed, and which therefore postdate the shearing. The older granitic and basic gneisses are traversed both longitudinally and transversely by shear-zones, so that these latter have clearly postdated the consolidation of the gneisses. It would appear, therefore, that the ore-

bodies were formed much later than the older gneisses and in connexion with some igneous intrusion which postdated the shearing. In an earlier paper(8) I attempted to show that the shear-zones were formed during a Proterozoic diastrophism. Mr. Andrews has shown that the loci of intrusion of the Mundi Mundi granites were controlled largely by the positions of these shear-zones, and it would appear at least possible that the silver-lead, zinc, copper and other deposits were introduced in connexion with these later more acid intrusions. Erosion has as yet revealed comparatively few and widely scattered outcrops of them, mostly well to the west of the meridian of Broken Hill, and it may be that the granite intrusions extend a long way over to the east of the existing outcrops but beneath the present surface. Actually many of the more western lodes are in at least as close contiguity to the Mundi Mundi granites as they are to the older gneisses. Nowadays it is recognised that in general ore-deposits like those of Broken Hill are emplaced either above or peripherally to the igneous intrusions with which they are connected, the ore-bearing emanations having travelled outwards or upwards beyond the limits reached by the main mass of magma. But the Broken Hill lode stands in neither of these relations to the older gneisses with which it is surrounded, and it and the outlying lodes might well be connected with an easterly underground extension of the Mundi Mundi granite.

It should be mentioned here that Mr. E. J. Kenny,* has arrived at practically the same conclusion as that enunciated above regarding the age of the mineralisation, and by similar reasoning. He, however, classes the Mundi Mundi granites as Archæozoic.

* Verbal communication from Mr. Kenny.

In Queensland in the areas where pre-Cambrian rocks outcrop age-relations between these and the ore-deposits do not seem to be always clear. A perusal of the Queensland Mineral Index reveals that titanium and beryllium minerals occur in some of the goldfields associated with pre-Cambrian rocks, but there is nothing on record as to the geological age of the igneous rocks with which they are connected.

Sir Edgeworth David[5] is of opinion that the hæmatite deposits of various parts of W.A., of Iron Knob, *etc.,* in S.A., and of the Cloncurry district (Q.), may have been derived from the magmas of the later granites.

IV. Metallogenetic and Petrographical Regions.

It has been suggested[5] that the late-Mosquito intrusive epoch was also Australia's most important metallogenetic epoch, and if the correlations indicated above are valid a great part of this continent was what might be called a late-Mosquito metallogenetic region, if such a region be defined as including the areas wherein during a given epoch of igneous activity the igneous intrusions or extrusions were accompanied by the magmatic deposition of ores. And if account be taken not merely of the ore-deposits but of the other common mineralogical and chemical peculiarities which have been enumerated above, the conclusion seems inevitable that these rocks were all derived from the same magma-reservoir, and that a good part of Australia constituted a great petrographical region in late-Mosquito time. As our knowledge of these rocks is increased it may be possible to recognise within the region a number of metallogenetic and petrographical provinces, each marked by some special peculiarity, chemical or mineralogical.

V. Former Extent of Lower Proterozoic Strata.

In a previous paper[8] the view was advanced that the presence of the outcrop of a bathylith implied the former existence of a sedimentary series, in connexion with whose folding and uplift the intrusion of the bathylith occurred. On such grounds the outcrops of the Mundi Mundi granite in the Barrier Ranges were considered to be evidence of the former presence in that region of a Lower Proterozoic series, the time-equivalents of the Mosquito Series of W.A. The argument may be extended considerably, for there are very large areas of late-Mosquito granite outcrops unaccompanied by sediments of Mosquito age. This point is emphasised by an inspection of the geological map of Australia, and apart from those beds which are buried beneath more recent deposits it would appear that the remnants of beds of Mosquito age which are left occupy only a very small fraction indeed of the area originally covered by the Lower Proterozoic sea and its sediments. That some of the enormous amount of implied erosion occurred during Proterozoic time is shown by the fact that the Mundi Mundi and Boolcamata granites are overlain directly by the sediments of the Upper Proterozoic Adelaide (Torrowangee) Series. The same is true for the Musgrave-Everard Range country and for some parts of W.A., showing that the late-Mosquito diastrophism was succeeded by pronounced uplift, and that a prolonged period of erosion preceded the deposition of the Upper Proterozoic strata.

VI. General Summary and Conclusion.

An attempt has been made to show that:

(1) An earlier and a later period of igneous intrusion accompanying orogenic movement may

be recognised in the pre-Cambrian throughout Australia;

(2) the intrusions of the first epoch (late-Archæozoic) were of the nature of synchronous gneissic intrusions with much *lit-par-lit* and stromalolithic injection, but without any distinctive mineralogical characteristics;

(3) the second series of intrusions was far more widespread and of far greater volume;

(4) the characteristics of these later intrusions indicate that much of Australia formed a metallogenetic and petrographical region in Proterozoic time;

(5) from the extent and distribution of these granites it is possible to deduce a former very wide extent of Lower Proterozoic strata in Australia, most of which have since disappeared through erosion.

Pre-Cambrian correlation in Australia, whether of sedimentary or igneous units, will probably never be final and beyond peradventure. Comparison of the sedimentary units will be mainly by the evidence of superposition, unconformities, lithology and degree of metamorphism. For the comparison of the igneous rocks peculiarities of mineral and chemical composition and even of structure provide criteria which may be suggestive and useful, though by no means final or infallible.

In the foregoing notes there is much that is tentative and hypothetical, but since in the absence of rigid criteria of correlation the methods of trial and error and of testing out hypotheses must necessarily be employed, it is hoped that this paper may serve a useful purpose.

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(In Nos. 2, 4 and 6 very full references to other literature will be found.)

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THE ESSENTIAL OIL FROM THE WOOD OF *EREMOPHILA MITCHELLI* (BENTHAM).

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(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

Eremophila Mitchelli is a tall shrub or small tree belonging to the *N.O. Myoporaceæ,* which attains a height of 20 to 30 feet and bears in the spring a wealth of white sweet-scented flowers. It is known vernacularly as Buddah Wood, Bastard Sandalwood or Budtha and its botanical characteristics are recorded in Bentham's "Flora Australiensis", Vol. 5, p. 21, and very graphically in Maiden's "Forest Flora of New South Wales", Vol. 7, p. 211. Its occurrence was apparently first observed by Sir Thomas L. Mitchell on January 9, 1846, at Muda, 26 miles south of Nyngan, on the Bogan River, New South Wales, and his interesting and original description is given in his "Tropical Australia", p. 31, published in 1848.

The tree, which has not been known to exceed a height of 25 to 30 feet, with a diameter of 12 inches at the butt, was stated by R. H. Cambage to be one of the strongest-scented woods of the western districts of New South Wales. It has been cut for commercial purposes and exported, presumably to the East. The Secretary of the Queensland Forest Service reported that 33 tons of wood

had been cut in Eidsvold and Hughenden districts of Queensland in 1924, but although royalties were paid, its destination was not known. The tree is found in the drier parts of New South Wales, Queensland and South Australia, although it is not entirely confined to these parts. In the western districts of New South Wales it is widely distributed, notably on the Bogan, Narran, Lachlan and Darling rivers. We are indebted to the Queensland Forest Service for an account of its distribution in Queensland: "*Eremophila Mitchelli* is a very common tree of western Queensland. It attains a maximum diameter of about 12 inches and is much more prevalent than *Santalum**, with which, on account of its name, sandalwood, it is often confused. The tree is found to the west of the Great Dividing Range, being recorded from Inglewood, Dalby and elsewhere in the Maranoa and Darling Downs districts, through inland areas to the west of Rockhampton and from Townsville to Charters Towers and Hughenden. It would be a valuable asset to this State if a market can be found."

The scented nature of its wood has been observed and commented on for many years, but it was not until 1923 that Dr. T. L. Bancroft, of Eidsvold, Queensland, submitted a log to the Technological Museum, Sydney, for investigation of its essential oil. The examination was commenced immediately, but the elucidation of its chemical constituents proved difficult and has only been completed recently. The oil will probably prove of economic value since a sample submitted to the Editor of "Perfumery and Essential Oil Record", was reported upon as follows (*Perf. Essent. Oil Rec.*, January, 1930, p. 30): "The oil is rather dark in colour and somewhat

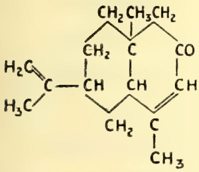
* *Santalum lanceolatum* is referred to.

viscid, and whilst it cannot provide the usefulness of sandalwood oil, it has remarkable qualities which place its value in line with those of fixative balsams. It has not a strong odour, but is soft with a suggestion of geranium to bergamot balsamic backing. Most noticeable is its agreeable character and its lasting quality on exposure in different atmospheres on paper strips, similarly when pounded into soap chips and exposed it was extremely persistent. The odour has a softening influence on those inclined to be harsh, even para-cresyl methyl ether was nicely subdued by it. Therefore, the oil has marked blending and fixative properties that should be found useful, particularly in the production of the cheap soap perfumes so much required to-day."

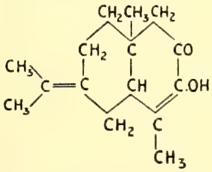
Since the submission of the first log, further logs have been received from Eidsvold, as well as from Tallabung, *via* Condobolin, Bourke, and Narrabri, New South Wales, and from the Queensland Forest Service from Dalby, Inglewood and Rockhampton. For the separation of the oil the logs were reduced to shavings, the plant at our disposal not being suitable for the production of sawdust, and the oil was removed by prolonged distillation in steam, the average yield being 2 to 3 per cent. Lower yields were obtained in many instances, but subsequent examination showed that this was due to the condition of the shavings. On a commercial scale the methods adopted for the manufacture of sandalwood oil from *Eucarya spicata* would have to be adopted.

The oils so obtained were in all cases dark reddish brown in colour, possessed a characteristic somewhat sweetish odour and were extremely viscid. As will be seen from the results recorded on p. 426, the constituents could not be separated by fractional distillation, but ultimately by methods to be described, three substances,

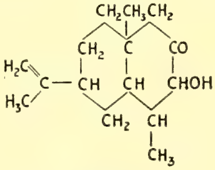
which form the main constituents of the oil, were separated: (i) a ketone, $C_{15}H_{22}O$, m.p. 41°–42°, for which the name *eremophilone* is proposed; (ii) a hydroxy ketone, *2-hydroxyeremophilone*, $C_{15}H_{22}O_2$, m.p. 66°–67°; and (iii) a second hydroxyketone, *2-hydroxy-2-dihydro-eremophilone*, $C_{15}H_{24}O_2$, m.p. 103°. On evidence which will be published elsewhere,* the ketones have been found to be represented by the following formulæ:



Eremophilone



2-Hydroxy-
eremophilone



2-Hydroxy-
2-dihydro-
eremophilone

Whilst eremophilone and 2-hydroxyeremophilone do not appear to have been described previously, it is probable that 2-hydroxy-2-dihydro-eremophilone occurs also in the oil from *Santalum Preissianum* from South Australia. In this connection see Gildemeister and Hoffmann's "The Volatile Oils", Vol. 2, p. 350, and also E. J. Parry's "Chemistry of Essential Oils and Artificial Perfumes", Vol. 1, p. 183. (*Santalum Preissianum* is now known as *Fusanus acuminatus*.)

For the separation of the ketones, two methods have been elaborated. The first depends on the observation that the oil is partially soluble in hot sodium bisulphite solution and after removal of the unreacted portion, which contains 2-hydroxy-2-dihydroeremophilone, the other two ketones can be regenerated by fractional

* The evidence upon which the structure of these substances is based, together with the analytical data for the ketones and their derivatives, will be published in a paper in the *Journal of the Chemical Society*, December, 1932.

decomposition with alkali, 2-hydroxyeremophilone being liberated first. This method of separation has two drawbacks, firstly, much of the ketones is lost, owing to the formation of soluble sulphonates, which are not decomposed by alkali, secondly the quantity of alkali required in each stage of the fractional decomposition varies, naturally, with different batches of the oil, since their composition is not identical. It is necessary, therefore, to determine the optimum conditions in each case. For the separation of large quantities of the ketones in a fairly pure condition it has, however, the advantage over the second process of being more expeditious. In the second process the oil, after a preliminary distillation to remove resinous material, is treated with an excess of semicarbazide acetate with which only eremophilone reacts readily. Eremophilone semicarbazone can then be isolated, purified by crystallisation and the ketone regenerated by hydrolysis with oxalic acid and steam distillation. From the oil which does not react with semicarbazide acetate, 2-hydroxyeremophilone was separated by taking advantage of the fact that it forms a crystalline benzoate, which is readily purified, and from which the pure ketone can be obtained by hydrolysis with alkali. This method has the advantage of yielding very pure products, but the steam distillations involved in the process (see p. 431) render it tedious.

In addition to the ketones referred to, the oil contains a small quantity of an unidentified sesquiterpene hydrocarbon, and other constituents, probably sesquiterpene alcohols, which have not been obtained pure. The percentage of these is, however, small.

These minor constituents will be more fully investigated at a later date.

Essential Oils from the Wood of Eremophila Mitchelli.

Date.	Locality.	Weight of Shavings	Yield of Oil.	$d\frac{15°}{15°}$	$n_D^{20°}$	$\alpha_D^{20°}$	Sol. in 70% Alcohol (by weight).	Ester No. 1½ hrs. Hot Sapon.	Moisture Content of Shavings
		lbs.	%						%
July 7, 1923..	1 Log from Dr. T. L. Bancroft, Eidsvold, Q.	12	3·3	1·0326	1·5291	Too dark.	3·6	120·0	18·8
September 9, 1923 ..	9 Logs from Dr. T. L. Bancroft, Eidsvold, Q.	259	2·2	1·0317	1·5260	,,	1·3	96·8	14·3
August 5, 1924	1 Log from Country Producer Selling Co., Sydney	3	1·3[1]	1·0418	1·5301	,,	2·2	—	
February 19, 1926 ..	6 Logs from A. Thierman, Tallabung, *viâ* Condobolin, N.S.W.	242	2·5	1·0276	1·5300	,,	3·3	42·0[2]	
August 27, 1929	2 Logs from R. P. Creagh, Bourke, N.S.W.	55	2·0	1·0381	1·5335	,,	4·1	—	
July 9, 1930..	Queensland Forest Service, Dalby, Q.	303	1·6[3]	1·0378	1·5365	,,	3·4	132·7	
September 23, 1930 ..	Queensland Forest Service, Inglewood, Q.	300	1·1[3]	1·0304	1·5328	,,	3·1	144·6	
November 19, 1930 ..	Dr. T. L. Bancroft, Eidsvold, Q.	379	1·2[3]	1·0383	1·5384	,,	10·0	53·7	
October 10, 1931 ..	6 Logs from Queensland Forest Service, Rockhampton, Q.	270	2·9	1·0304	1·5326	−6° (approx.)	4·0	113·2	
May 5, 1932..	G. Burrow, Narrabri, N.S.W.	140	1·0[1]	1·0343	1·5327	+6°	3·3	17·0	20·5

[1] Low yield due to preponderance of sapwood over heartwood.
[2] Acid value, 4.
[3] Yield low, due to incomplete removal of oil brought about by long storage of sawdust before distillation.

Experimental.

Shavings (1,963 lbs.) obtained from logs from various localities in New South Wales and Queensland were subjected to steam distillation and the oils examined, with the results shown in Table I. It will be observed that the physical constants show comparatively little variation although the ester value and the solubilities in alcohol show marked differences. Unfortunately the oils were, in most cases, too deeply coloured for the optical rotatory power to be determined. Although, as already mentioned, the constituents of the oil could not be separated by fractional distillation, it is of interest to record the results obtained in one distillation, 300 c.c. of oil being used.

Table II.

No.	B.P. (3 mm.).	$d_{15°}^{15°}$	$n_D^{20°}$	$\alpha_D^{20°}$	Yield.
1	Up to 130°	0·9859	1·5169	−63·0°	20 c.c.
2	130°–140°	1·0164	1·5252	−55·2°	37 c.c.
3	140°–150°	1·0203	1·5280	−45·2°	80 c.c.
4	150°–153°	1·0297	1·5346	− 9·2°	100 c.c.
	Residue 40 c.c.				

Fraction 4 was redistilled with the following results:

Table III.

No.	B.P. (3 mm.).	$d_{15°}^{15°}$	$n_D^{20°}$	$\alpha_D^{20°}$	Yield.
4A	Below 153°	1·0205	1·5260	−51·0°	12 c.c.
4B	153°–155°	1·0281	1·5328	−21·5°	65 c.c.
4C	Residue	1·0486	1·5455	+61·6°	16 c.c.

Separation of Eremophilone, 2-hydroxyeremophilone and 2-hydroxy-2-dihydroeremophilone.

Method I. With Sodium Bisulphite.

A mixture of the crude oil (100 c.c.), sodium bisulphite (60 g.), and water (200 c.c.) was boiled under reflux for two hours, one hour being required for complete emulsification. The cooled solution was extracted with ether to remove unreacted oil and then treated with a large excess of sodium hydroxide solution (20%), when the ketone separated. This was dissolved in ether, the ethereal extract dried and the solvent evaporated. A viscid yellow oil was obtained which was purified by distillation under diminished pressure, when it was found that the ketone from different preparations showed varying properties, as will be seen from the following typical results.

TABLE IV.

	I.	II.	III.	IV.	V.
b.p.	157°–158°/ 4 mm.	159°–160°/ 6 mm.	160°–163°/ 5 mm.	—	—
$d_{15°}^{15°}$	1·007	1·0058	1·024 –1·0316	1·0333	1·0058
$n_D^{20°}$	1·524	1·5224	1·5332–1·5375	1·5381	1·5219
$\alpha_D^{20°}$	−144°	−168·6°	−28° to −53°	−9·6°	−162·4°

(Fraction 3 refers to different samples of the same b.p. prepared from Rockhampton wood 7/10/31.)

The separation of fractions having approximately the same b.p., but showing such wide differences in their rotatory power, suggested the presence of two ketones, although it also appeared possible that the change in rotatory power might have been due to partial racemisa-

tion during the distillation. The variation in the refractive index (1·5220 to 1·5380) did not, however, support this view. Ultimately the separation of a *dextro*- and a *lævo*-rotatory ketone was accomplished by the comparatively simple process described below.

In one experiment the crude oil (400 c.c.) from the Rockhampton wood was digested as described above with sodium bisulphite solution, and, after removal of the unreacted oil, the bisulphite solution was treated with successive quantities of sodium hydroxide solution (25%), when four fractions of ketone were obtained, the results being summarised in Table V.

TABLE V.

No.	NaOH Added.	Yield of Ketone.	$\alpha_D^{20°}$
1	250 c.c.	67·5 g.	Solidified before constants could be determined.
2	250 c.c.	44·0 g.	−106·8°
3	250 c.c.	44·5 g.	−148·0°
4	500 c.c.	4·5 g.	−100·0°

A sample of oil (100 c.c.) from the Narrabri wood was treated similarly with the results shown in Table VI.

TABLE VI.

No.	NaOH Added.	Yield of Ketone.	$n_D^{20°}$	$\alpha_D^{20°}$
1	200 c.c.	11·0 g.	1·5395	+ 17·2°
2	200 c.c.	12·0 g.	1·5276	−102·0°
3	200 c.c.	9·5 g.	1·5229	−164·0°
4	250 c.c.	2·5 g.	1·5266	−142·0°

Eremophilone.

This ketone was readily isolated from fractions 2 and 3 (Table V) and from fractions 3 and 4 (Table VI). These fractions were freed from a little resinous matter by distillation under diminished pressure, when fraction 3 (Table VI) had the following constants: b.p. 157°–158°/4 mm., $d_{15°}^{15°}$ 1·0058, $n_D^{20°}$ 1·5224, α_D–168·6°. Fractions 2 and 3 (Table V) crystallised almost at once after distillation, the solid having m.p. 35°–36°, $[\alpha]_D$–139·5° (in chloroform). The solid was freed from oil by filtration and recrystallised from ice-cold methyl alcohol, when it separated in long prismatic needles, m.p. 42°–43°, $[\alpha]_D$–171·6° (in ethyl alcohol), $[\alpha]_{5461}$–207° (in methyl alcohol). As mentioned already, eremophilone has the composition $C_{15}H_{22}O$, and its alcoholic solution gives no colour with ferric chloride.

2-Hydroxyeremophilone.

For the separation of this hydroxy-ketone fraction 1 (Table V) (62·5 g.) was freed from oil by suction at the pump when the crystalline solid which remained (38 g.) was readily purified by recrystallisation from methyl alcohol, from which it separated in prisms, m.p. 66°–67°. In chloroform solution it had $[\alpha]_D + 140·5°$ and in methyl alcohol solution $[\alpha]_{5461} + 153°$. This hydroxy-ketone, $C_{15}H_{22}O_2$, differs from eremophilone in that its alcoholic solution gives with ferric chloride an intense brownish-black coloration. The same ketone was isolated from fraction 1 (Table VI).

2-Hydroxy-2-dihydroeremophilone.

The oil, which did not react with sodium bisulphite, crystallised partially on keeping in the ice chest for 24 hours. The solid was collected at the pump, drained on

porous porcelain to remove adhering oil and purified by repeated crystallisation from methyl alcohol, when it was obtained in very beautiful long prisms, m.p. 102°–103°, $[\alpha]_D$ + 90·6° (in chloroform), $[\alpha]_{5461}$ + 94° (in methyl alcohol), having the composition $C_{15}H_{24}O_2$. This substance was also isolated direct from the crude oil distilled from logs from Inglewood, 23/9/30. The oil on standing in the ice chest for several days deposited over 70 grams of the crude hydroxyketone.

Method II. With Semicarbazide Acetate.

To an aqueous solution of semicarbazide hydrochloride (35 g.) and sodium acetate (40 g.) the crude oil (Inglewood), freed from resin by distillation under diminished pressure, was added, together with sufficient alcohol to give a clear solution. After remaining at room temperature for three days, the alcohol was removed on the water bath and the residue poured into water. After standing for some hours the clear aqueous solution was decanted from the gum, which was washed several times with water and then transferred to a bottle and shaken mechanically with a small quantity of sodium hydroxide solution and light petroleum for two hours. A considerable volume of light petroleum was then added and the agitation continued for a further three hours. The solvents were decanted from the gum, which was washed with water and allowed to remain overnight with a fresh quantity of light petroleum. The gum, which was now mainly crystalline, was collected at the pump, washed with light petroleum and dissolved in the minimum quantity of hot methyl alcohol, when, on standing, a colourless crystalline solid was deposited, consisting of nearly pure *eremophilone semicarbazone.* (Yield 13 g.)

The combined light petroleum washings were well washed with water, dilute sulphuric acid, once more with water, dried and allowed to stand, when a further quantity of eremophilone semicarbazone (6 g.) separated.

In another experiment using Rockhampton oil (third distillate) (100 g.) 27 g. of eremophilone semicarbazone were obtained. A further quantity of the nearly pure semicarbazone can be isolated by fractional precipitation from the methyl alcohol mother liquors by the addition of water. Eremophilone semicarbazone crystallises from methyl alcohol in concentric clusters of needles m.p. 202°–203°.

For the preparation of the pure ketone the semicarbazone was suspended in water, and after the addition of a slight excess of oxalic acid and a small quantity of alcohol the mixture was heated on the water bath under reflux for two hours. The liberated ketone was then removed in steam, the yield being quantitative. Eremophilone so obtained was an almost colourless oil b.p. 171°/15 mm., $d_{25^\circ}^{25^\circ}$ 0·9994, $n_D^{25^\circ}$ 1·5182, α_{5461}–184°, α_{5780}–158°, which on inoculation crystallised in needles and was identical with the ketone prepared as described on p. 429. The optical rotatory power was found to vary somewhat in different preparations, the lowest observed value being $[\alpha]_{5461}$–132° (in methyl alcohol), and the highest $[\alpha]_{5461}$–207° (in methyl alcohol). This was not due to the presence of 2-hydroxyeremophilone since the ketone gave no colour with ferric chloride in alcohol solution.

The light petroleum solutions from several such preparations of the semi-carbazone were combined, the solvent removed and the residual oil distilled in steam, some twenty litres of water being required for 60 g. of oil. The residue in the distillation flask was a red

resin from which a further quantity of eremophilone could be obtained by hydrolysis with oxalic acid, as described above.

The oil (60 g.), which was volatile in steam, was isolated by extraction with ether in the usual manner and purified by distillation under diminished pressure (20 mm.), when the following fractions were obtained: (i), 175°–180° (11 g.); (ii), 180°–185° (8 g.); (iii), 185°–195° (37 g.). Fraction (1) was repeatedly refractionated when ultimately a fraction b.p. 150°–153°/24 mm. was obtained which analysis (found: C, 85·5, H, 11·3%) showed to consist essentially of a hydrocarbon. It had the following constants: $d_{25^\circ}^{25^\circ}$ 0·9354, $n_D^{25^\circ}$ 1·5033. Attempts to prepare crystalline derivatives have so far proved unsuccessful.

Fraction (iii), b.p. 185°–195°/20 mm., consisted essentially of 2-hydroxyeremophilone; on redistillation it passed over almost completely at 188°–190°/23 mm. as a pale yellow oil giving an intense colour with ferric chloride in alcoholic solution. For the preparation of pure 2-hydroxyeremophilone, the oil (20 g.) was dissolved in dry pyridine (70 c.c.) and to the cooled solution (salt-ice) benzoyl chloride (13 g.) was gradually added. After remaining overnight the reaction mixture was heated on the water bath for one hour, cooled and poured on to ice. The red oil which separated was dissolved in ether, the ethereal solution washed successively with water, dilute sulphuric acid, sodium carbonate solution and water, dried over calcium chloride and the solvent removed. The residual oil was distilled in a high vacuum (1 to 2 mm.) when, after a small fraction had passed over below 200°, the greater part distilled at 200°–220° as a viscid gelatinous oil. This was dissolved in hot methyl alcohol and the colour-

less crystalline solid, which separated on cooling, collected. *2-Hydroxyeremophilone benzoate*, m.p. 119°–120°, crystallised in glistening prisms. By the hydrolysis of the benzoate with alcoholic potassium hydroxide in the usual manner, 2-hydroxyeremophilone was obtained as a very viscid, pale yellow oil, b.p. 189°–190°/22 mm., $d_{25°}^{25°}$ 1·0620, $n_D^{25°}$ 1·5564, $[\alpha]_{5461} + 153°$ (in methyl alcohol). It crystallised on inoculation and was identical in all respects with the hydroxyketone described on p. 429.

The methyl alcoholic solution from which the crystalline benzoate had been separated contained a liquid benzoyl derivative. This was hydrolysed with an alcoholic solution of potassium hydroxide and the product, isolated in the usual manner, was an oil, which on distillation under diminished pressure (20 mm.), was separated into two fractions: (i), b.p. 175°–180°, $n_D^{25°}$ 1·5275, $[\alpha]_{5461} + 67°$ (in methyl alcohol); (ii), b.p. 180°–185°, $n_D^{25°}$ 1·5372. The quantity of the two oils was insufficient for further investigation.

We are indebted to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries for grants which have in part defrayed the cost of this investigation.

Our thanks are due to Mr. F. R. Morrison, A.A.C.I., Assistant Economic Chemist, Sydney Technological Museum, for much assistance in the distillation of the oils from the wood and the determination of the chemical and physical constant of the crude oils.

We are also greatly indebted to many friends who furnished supplies of raw material, particularly Dr. T. L. Bancroft, Eidsvold, Q., the Queensland Forest Service, and Mr. Gordon Burrow, District Forester, Narrabri, N.S.W.

AN EXAMINATION OF THE VALIDITY OF CONCLUSIONS DRAWN FROM EXPERIMENTS IN WHICH THE ALLANTOIC MEMBRANE OF THE CHICK IS EXPOSED TO X RADIATION.*

By WARNFORD MOPPETT, M.D., Ch.M.

(With Plate IX and Seven Text-figures.)

(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

INTRODUCTION.

In a thesis[1] on the reaction of the allantoic membrane of the chick to homogeneous X radiation produced by crystal diffraction, there were two main objects, "adapting the X ray spectrometer to biological purposes and obtaining and proving X ray effects" and "seeing whether such effects occurred uniformly or selectively at certain wave lengths."

The first requirement involves a very fundamental discovery because the energy available is extremely small, whilst there is no extraordinary sensitivity to mixed radiation.

To establish selective action, the X ray spectrum was explored in duplicate from 0·1 to 1 Å. at approximately 0·1 Å. intervals. These separate series of experiments were also made by different and simpler methods. In a later paper[2] a systematic exploration from 0·3 to 1 Å. at 0·05 Å. intervals was included and investigation was extended to 2 Å. Of a total of 120 experiments only 3 were inconsistent with the graphical representation employed and the experimental aspect of selective action is a probability which is indicated roughly by the factor 117/120, apart from supplementary evidence.

* This work was carried out under the control of the Cancer Research Committee of the University of Sydney and with the aid of the Cancer Research and Treatment Fund.

It was thought advisable at this stage to work on various other problems, Antagonism,[3] Area,[4] Time,[5] which called for investigation partly because they appeared necessary to solve certain practical problems of selective action and partly because of their possibly greater intrinsic importance.

Mouse skin, frog skin and *in vitro* cultures[6] were exposed to homogeneous rays to determine the scope of the work and finally tumour tissues[7] were exposed to a graduated series of radiations of varying homogeneity to indicate the possibility of future clinical application.

All the above extensions of the original problem depend on the first and more fundamental objective in the thesis, for which the evidence is conclusive. Although independent in this way of "selective action" there can be no doubt that all the phenomena are different forms of the one problem.

About a year ago, on the completion of a radiometer,[8] matters were favourable for resuming work on the allantoic membrane, and the question arose whether it was better to commence a new problem or to revise the older work since, unfortunately, there had been no serious attempt to repeat any of the experiments elsewhere.

By a happy compromise it was possible to combine the two aspects, but before describing experiments I will outline and discuss some of the points raised in the previous work.[2]

1. Control egg windows should show no reaction.
2. Homogeneous radiation in suitable dose should cause a reaction.
3. Mixed radiation in a much larger dose should cause no reaction.
4. A small dose of (homogeneous) radiation causes no reaction.
5. An intermediate dose of (homogeneous) radiation causes hypertrophy or stimulation.
6. A large dose of (homogeneous) radiation causes atrophy or destruction.
7. Selective action.

Etc.

Commenting on the above:

1. Controls imply those eggs from which "windows" were removed in the manner described[2] and which as far as possible were treated at the same time and in the same manner as the corresponding irradiated specimen. During the investigation of selective action 30 were employed (one to every four experi-

ments), mainly in groups at the early part of each exploration of the spectrum.

None of the above showed any reaction and some were of special value as they reposed in the second compartment of a hot box used for irradiation.[2] If one assigns the probability of ½ to the right interpretation of a single experiment the chance of error in 30 consistent experiments is 1/100,000,000.

It was known, however, at quite an early stage that specimens in which the window was kept open for say 12 hours or 6 times the usual period, might show small nodular thickenings situated peripherally near the shell margin and suggesting reaction to the injury of cutting the window. Such long exposures raised the usual mortality of 30% to over 90% and this work was discontinued until recently, when long exposures were required for the investigation of β ray action.[9] Marginal reactions were obtained here, but experience and perfection of technique enabled one to obtain some controls which showed no reaction after 4 days' continuous exposure. Subsequent experience has shown that the antiseptic effect of a slow leakage of emanation may have been of assistance.

2. During the first few weeks of my systematic exposure of prepared eggs to homogeneous radiation, I obtained small round nodular thickening in the allantoic membrane which bore so little relation to the cross section of the incident beam that I doubted the causal relationship of the radiation. I was convinced when, after a long series of dead specimens, I obtained large reactions approximating to the contour of the spectrometer slit at what appear to be the more effective wave lengths. Later on I had great difficulty in producing "geometrical" reactions, and a laborious research showed that firstly an adequate dose was necessary because a small dose tends to give the nodular reaction in the centre of the irradiated area. It was also found that there was an overflow of reaction and a rounding off of angles so that geometrical reactions could only be produced on a certain minimal scale of size. For some time it was the practice to turn the egg window so that the incident beam would fall obliquely and cover a large area.

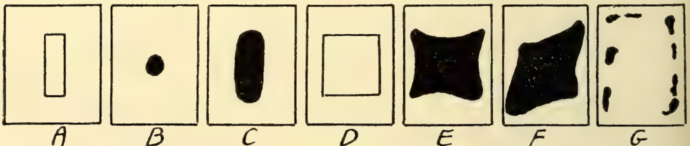


Fig. 1.

In the above Fig. 1, A represents the incident beam, B the small central nodule, C the "geometrical" reaction at normal incidence, D the incident beam at oblique incidence, E the reaction distorted owing to the curvature of the egg, and F the further distortion obtained because an egg naturally lies at a slope ([2], Fig. 3). The latter obliquity was often deliberately emphasised as a contrast to spurious reactions, G, which tend to run parallel to the shell margin.

I will not discuss microscopic appearances in this paper because it is a first essential that any reaction should be satisfactory from the point of a general naked eye view. To quote from the thesis, "the reaction should be centrally placed (unless the rays are directed elsewhere) and surrounded on all sides by normal membrane continuous over the sawcuts in the shell."

A perusal of my previous papers[2][3][4][5] will show that a considerable number of reactions have been obtained in the allantoic membrane attributable to homogeneous radiation. There is a small variation in individual sensitivity expressed as a variation of 20% to 30% in threshold dose, and keeping the energy within such limits one would obtain equal numbers of reactions and blanks. It is also easy to place the egg in a faulty position so that the rays partly or entirely miss the window, but with wider experience it was found that a reaction is always produced if the dose is adequate. About 27% of the exposed specimens showed no reaction but only consistent with an inadequate dose or non-effective wave length.

3. Although the exposures to mixed radiation were rather few in number, the resistance is so great compared with that of homogeneous radiation, 1,000/1, that any failure to react was a most arresting phenomenon.

Of course, with sufficient dose one could produce mixed ray reaction, but I wrongly supposed that the atrophic reaction[2] was characteristic of homogeneous radiation only. At the suggestion of Professor Vonwiller I gave a series of short exposures to mixed radiation without result to exclude a zone phenomenon.

4 and 5. Number 4 requires no explanation, but it will be necessary to define carefully the meaning of the word stimulation in Number 5. Firstly, it is not to be confused with the word stimulus as used by physiologists. Stimulation implies increased activity (as a result of a stimulus) but the meaning is here restricted to mitotic activity resulting in the production of new cells. It is quite unnecessary to demonstrate mitosis

because there is an obvious increase in the number of cells of both mesenchyme and epithelia as compared with the average or undisturbed condition.

I would be more cautious in distinguishing between primary stimulation and stimulation secondary to injury, that is cellular destruction and not a hypothetical physico-chemical injury. The evidence for the former is the quick appearance of the reaction (in three days) and its steady growth over shorter periods. There is also an absence of microscopic evidence of degenerative change in many examples of small and purely hypertrophic reactions.

6. No one will doubt that any intense stimulus applied to living tissue will produce atrophy or necrosis, and this is well borne out in the X ray effects where the membrane may wither to an amorphous sheet in 4 days. There is a doubt, however, as to whether atrophy is primary or secondary to nutritional disturbance.

I will not digress from the scope of this paper by a discussion of the above, beyond the statement that both factors play a part. I will also avoid the question of atrophy or hypertrophy producing wave lengths and assume that the radiation under discussion will first produce hypertrophy and then atrophy. This furnishes two thresholds for purposes of measuring, but owing to the complication of nutritional change, the atrophic threshold may be less constant than the hypertrophic threshold which was employed for what I consider my most precise investigations.[3]

7. I have already discussed the experimental aspect of selective action, but there is another aspect involving selective action as a deduction after considering questions of energy, absorption, *et cetera*. In the case of the present revision, it is desirable for clarity to keep the two aspects separate.

Experiments.

I commenced work on mixed radiation because some amplification of previous data was desirable and it was also a convenient preliminary to a further study of homogeneous radiation. I was in a position to measure total energy in absolute units,[8] and the first point was to confirm an observation[3] that the threshold dose varies with the energy distribution. I also hoped to obtain

indirect evidence of selective action in the region above 100 KV., which is of clinical importance but inconvenient for the method of crystal diffraction.

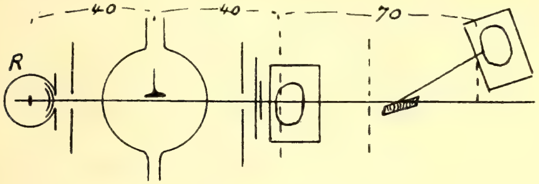


Fig. 2.

A window was made in an egg[2] and this was placed in a hot box situated symmetrically opposite to the radiometer R (Fig. 2), the tube presenting a line source at grazing incidence in either direction. The egg was screened by a filter of 0·03 cm. aluminium, 0·3 cm. (monax) glass to reproduce the radiometer coverings and the incident beam passed through a rectangular aperture 1 × 0·5 cm. (Plate IX, Fig. 12). The method of operation was to vary the voltage (from 90 to 150 KV.) and keep the total incident energy constant by adjustment of the milliampèrage. A Gaiffe Gallot constant potential generator and water-cooled Coolidge tube were employed. Previously it has been shown that the total energy varies directly as the milliampèrage and as the square of the potential.[10] It was therefore necessary to satisfy the following condition: CV^2 = constant, and check readings were taken with the radiometer which showed a galvanometer deflection of 6 mm. for the first series of experiments. Voltage was measured as before,[10] by taking the kilovoltmeter reading when a spark first passed. The gap was then opened slightly and the kilovoltmeter kept at the desired setting provided the input voltage remained constant.

A graduated series of exposures was given from $\frac{1}{4}$ to $1\frac{1}{4}$ hours at each voltage, and the results are recorded in Fig. 3, where the open circles represent blanks, the closed circles reaction and the half-blackened circles doubtful or slight reactions.

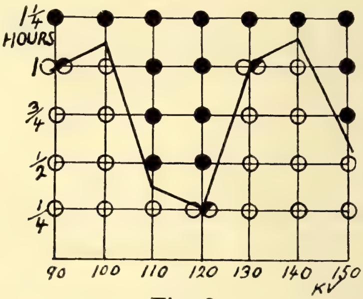


Fig. 3.

The results were so striking that I decided to attempt repetition at once, but I was delayed by a mechanical breakdown which led to subsequent differences and irregularities. About this time Dr. Hunt showed me that reactions could be obtained after a comparatively short exposure (two hours) under certain conditions without

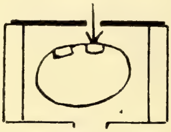


Fig. 4.

irradiation. To be on the safe side, I placed a second or control window (Fig. 4) in the confirmatory experiments (Fig. 5).

No spurious reactions were obtained, but the winter had now set in, with a resulting heavy mortality, so that there were considerable intervals during the building of graphs (Fig. 5), and lack of time prevented its completion.

The correspondence of 3 and 5 is, however, good, the apparent sensitivity being less and the galvanometer reading more (7 mm.) in the second series. This only means that the tube was rotated slightly towards the

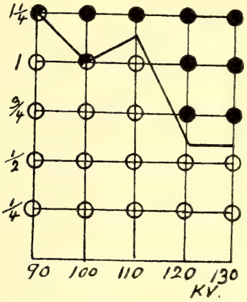


Fig. 5.

radiometer during repair work. (The apparent displacement of maximum action by 10 KV. is due to unsteady operation in an old gassy tube, when the average effective voltage is less than the nominal.)

The total incident energy per sq. cm. (the irradiated area = ½ sq. cm.) may be obtained from the deflection (6 mm.) and data previously obtained with the radiometer[8] taking a period of 1 hour.

A series of six unpublished deflection readings (a null method was used mainly[8]) gave a value of 1·40 cm. with a probable error of 0·025 cm. under certain constant conditions.

A series of alternating readings was taken in a similar manner to determine the total energy (E) in ergs per sq. cm. per second from the relation

$$E = V \frac{ajms}{b}$$

where V is proportional to the deflection and the other symbols have the meaning assigned in the previous

paper,[8] where E was determined as 600 ergs per sq. cm. per second.

Therefore an hour's exposure at 0·6 cm. deflection corresponds to a total incident energy $9{\cdot}25 \times 10^5$ ergs, by far the most accurate estimate made in connection with my work.

During the course of this investigation, I observed hypertrophic and atrophic reactions (corresponding to small or large effects) which were indistinguishable to the naked eye from those obtained with homogeneous radiation. Previously I had not obtained atrophy with mixed radiation, and thinking it might be a matter of voltage, I tried some experiments with a universal tube at 30 KV., 3 m.a. const. pot., 15 cm. By irradiating an area of $1 \times 0{\cdot}5$ cm. (much larger than previously), I obtained typical atrophies with exposures of 2 hours and over and a careful microscopic check was made. I will also describe typical atrophy in a spurious reaction, so that this condition is a general type of response not associated with any particular form of stimulus.

Fig. 6.

Before leaving the subject of mixed radiation I made a check of the possibility of a zone phenomenon by giving a very small dose over a long period of time—1 hour. The primary beam was scattered (at right angles) from a paraffin block as shown in Fig. 6. The rays passed on to the egg through a slit-like aperture and careful photographic checks were made giving roughly $\frac{1}{360}$ the initial intensity (3×10^3 ergs per sq. cm.).

The scattered radiation is practically similar in composition to the primary beam and 3 negative experiments appeared to furnish a definite answer in respect of the above conditions. Previously[2] one obtained a reaction from scattering when the crystal was placed out of alignment. The most likely explanation is associated with a predominant effective frequency excited by fluorescence. However, this work is concerned with a "deduction" termed "antagonism" which lies outside the scope of the present paper.

A simultaneous investigation has been made to gather further information into the significance of making a shell window. Firstly, incubated eggs were exposed to the direct mixed rays through intact shell. Conditions and dosage were varied giving a final result of 8 dead, 2 blank, 6 reactions. The latter were less exuberant than those obtained with windows, but the geometrical outline of the slit was very well reproduced, usually as a pale bloodless area (Plate IX, Fig. 8), leaving no doubt as to causal relationship.

Microscopic section showed both hypertrophic (Fig. 9) and atrophic changes according to conditions, but in accordance with the observation already made, these were less extensive. The threshold was reached in about 1 hour at 140 KV. and 10 m.a. (deflection 1·8 cm. average) and the total energy incident on the outside of the shell would be 3×10^6 ergs per sq. cm.

I then thought that it might be possible to obtain homogeneous ray reactions through intact shell if I used a hard radiation when loss in the shell and change of wave length by fluorescent absorption would be relatively unimportant. The wave length used was 0·128 KV., in the hard continuous spectrum beyond the K lines of

tungsten and the requisite high resolution was obtained with 1 mm. slits arranged as in Fig. 2. A two and three hours' exposure were unfortunately both negative so that this investigation is not promising.

The distance was increased from 40 cm. for the mixed ray to 110 cm. and, allowing an efficiency of 10^{-3} for the crystal, the energy for (1·8 cm. deflection) and 3 hours is roughly

$3 \times 10^6 \times 3 \times 10^{-3} \times (\frac{40}{110})^2$ or $1 \cdot 3 \times 10^3$ ergs per sq. cm. the irradiated area being much smaller.

For purposes of demonstration I then set the instrument to give a wave length of 0·53 Å. (with 3 mm. slits) and an excellent "geometrical" reaction was obtained in a "window" (Plate IX, Figs. 10 and 11). Calculation would give the same value per hour for total incident energy per sq. cm. and the exposure of 1 hour employed represents 4×10^2 ergs.

Dr. Hunt very kindly showed me the reactions she obtained in non-irradiated specimens by exposing the shell windows for 2 and 3 hours in her stock incubator. Previously I had only obtained occasional spurious effects after exposures of 12 hours or more. The less intense radiations obtained by Dr. Hunt were marginal in accord with my observation, Fig. 1, but more intense effects tended to become central when they looked very like some X ray reactions. I soon observed that several apparently atrophic reactions were really marginal hypertrophies with a normal or unchanged centre. In other cases the centre withered producing true atrophy apparently secondary to a disturbance of nutrition.

Dr. Hunt used a very small window, 1 × 1 cm. (much too small for X ray work), and I have found that reactions can "creep" for distances of a few millimetres.[(4)] Thus I

regard her effects as primarily marginal but forced to resemble central reactions by cramped surroundings. I then invited the occurrence of spurious reactions by exposing a large number of prepared eggs in my stock incubator. The window was made 2 cm. square (removed in four pieces) in order to distinguish the site of origin of reaction. Deaths accounted for 20 experiments while one specimen each was obtained for 1 and 2 and 3 days' exposure followed by immediate fixation.

The 1-day specimen was unchanged, the 2-day slightly altered in appearance, and the 3-day had an intense marginal response and a patchy distribution of atrophy and hypertrophy all over the central area. There was strong evidence of infection, so I sterilised the incubator and determined that all future exposures should be made in a separate enclosure.

There was also a possibility of dehydration playing a part and I exposed 6 specimens with large windows for 24 hours in a calcium chloride desiccator. One survived (normal) and the dead ones showed remarkably little alteration in contrast to the usual signs of decomposition which are prominent even in 24 hours.

The next step involved rough tests with a hygrometer which showed that my incubator (bacterial type) had an average humidity of 60% or 70% if a tray of water was used. This compared very well with the 55% humidity recommended by poultry farmers during the second week of incubation. Tests were made in the small hot box used for irradiation and the average was found to be about 60% though subject to greater inaccuracy and variation than the above determination. This was completed just as the mortality began to rise with the winter months, but work was continued partly

because it was felt that the results would be more valuable under the comparatively unfavourable circumstances.

Three grades of humidity were provided for in separate enclosures—a jar containing a smaller vessel of water (100%), the desiccator which would provide about 20% above zero owing to a continual outflow of moisture from the egg, and finally the irradiation hot box[2] and (60%) which would reproduce experimental conditions apart from the small amount of nitrogen oxide given off by an X ray plant. The latter was included in the control windows already described and no reaction was produced in exposures up to 1¼ hours.

The results after sealing and incubation for 3 days were as follows:

Moist.—(6 hours' exposure) 1 dead, (3 hours' exposure) 14 dead, 10 blank.

Desiccator.—(6 hours' exposure) 15 dead, (3 hours' exposure) 19 dead, 9 blank.

Irradiation Box.—(6 hours' exposure) 9 dead, (3 hours' exposure) 24 dead, 14 blank, 1 slight reaction.

The above showed that dehydration played no part and a clue to a source of infection was supplied when I noticed that the reacting specimen had touched some cotton wool that had not been changed for some time. With strong evidence for an infective origin of spurious reactions there remained the question of mechanical injury and the peculiar peripheral distribution noted.

Sharp angular beads were pressed on to the exposed shell membrane by wiring and waxing down a shell cover and incubation was continued for three days. The results showed 13 dead and 5 blank, which proved that continued mechanical pressure does not cause a reaction,

whilst it is generally agreed that the momentary injury of opening and sealing a window causes no change.

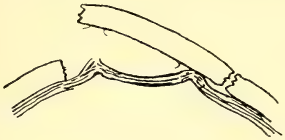


Fig. 7.

The probable solution was found by watching the receding shell membrane as one lifts up a shell fragment. There is a point of greatest flexion and strain about 2 mm. from the cut edge (Fig. 7). This explains why organisms do not pass through the intact shell or through very carefully made windows. The mechanical injury is necessary but it acts indirectly by providing a free passage to the allantois.

I had an impression that heavy mortality and spurious reactions are associated. Possibly they are in that heavy mortality implies a lower vitality or a less perfect formation of the egg leading to more easy infection. One has not isolated a common infective agent. Professor Wright and Dr. Goldsworthy kindly examined an egg which appeared much decomposed, but the material was sterile both for bacteria and moulds. I confirmed this indirectly by inoculating material from such an egg on to exposed shell membrane. I obtained 3 dead and 3 blank which may be interpreted as showing the procedure produced no change.

The evidence for an infective agent in the case of the spurious reaction is much stronger. In my dead specimens I saw two mould growths, one in the moist enclosure and one in the stock incubator, the latter case showing a cast in mycelium of the subjacent necrotic allantoic membrane.

Sealing up a window with some "dirty" cotton wool for 3 days certainly did produce a reaction—13 dead, 3 reactions, 2 slight reactions, and 1 blank. The dead specimens were either coagulated in a peculiar manner or in an extreme state of liquefaction. I am not suggesting that the wool is always the source of the infection which must come with the supplies from the poultry farmers. A stray piece of wool forms a convenient inoculating instrument and in my previous work I always avoided such contact. I suspected an infective origin of dead specimens and as a matter of course changed cotton wool and sterilised containers at frequent intervals and immersed all discarded biological material in lysol solution. I have often hoped to avoid complication by painting the newly made window with vaseline *et cetera*, which gives the advantage of visibility during development. Unfortunately I confirmed my former conclusion that this causes a very high mortality —4 dead, 1 blank—but further investigation with pure paraffin is needed.

Conclusions.

I will speak in terms of the seven points previously mentioned, of which the first three—controls, homogeneous radiation, mixed radiation—are fundamental.

A simultaneous solution is really required but the relative resistance to mixed radiation has now been proved beyond all doubt and I wish to establish the causal relationship of the homogeneous ray reaction in terms of the first two observations.

The discrepancy between my blank controls and Dr. Hunt's experiments (wrongly termed controls) is due to a difference in treatment, apparently small, but as it happens, essential.

By exposing large numbers of treated eggs in the stock incubator Dr. Hunt provided a breeding ground for the first stray organism (asepsis is impossible where new supplies of

living material are being added) and the numbers were increased and the virulence exalted by the ample pabulum. I have been put to the inconvenience of taking quite unusual precautions to obtain the above results because the laboratory previously clean has been infected by air-borne spores. Dr. Hunt has very kindly permitted me to quote her work, and I think her negative results with the window downward, and positive up to the air, are almost conclusive on this point.

I have advanced the view that there are two factors involved, a mechanical opening up of the shell membrane (Fig. 7) and the presence of a suitable organism. This explains the advantage of a gentle technique (and also a simple one) and the comparatively small numbers used in my irradiation work (twelve per week) will explain why my controls were 100% negative—that is it would be rare under the circumstances to obtain a coincidence of both factors.

I suppose care will always be needed because the allantois is a sensitive structure, fifteen times as much as mouse skin,[6] but is there any evidence for a lack of reliability? Quite large doses of mixed radiation produce no change, neither does mechanical distortion for 3 days, dehydration for 3 hours or 100% humidity plus partial asphyxia for a similar period. (The last named showed a comparatively low mortality.) On the other hand the sensitivity is an advantage which just makes work with crystal diffraction convenient and possible. The perfect fixity of the membrane is also a great help and the comparative simplicity of its tissues may serve to furnish a clue to the more complex problems of mature mammalian tissues.

Is there any reason to doubt the validity of my previous results? Apart from the thirty consistent controls it seems impossible that an unknown factor should simulate a selective effect which was duplicated in five series of experiments. It may be mentioned that one does not fill a graph in progressive steps but deaths force one to take the safer course of jumping about from place to place. My later work—antagonism *et cetera*—was not associated with separate controls, but the position is even more secure because the experiments were in general carried out in pairs, exposed for the same time but at different intensities of which the greater caused a reaction. Not only was the chance of obtaining a spurious effect remote, but the chance of confusion with the X ray effect was still less probable.

With a good technique, a reasonably large window, and clean (non-infective) conditions the spurious effects (as in my β ray work) were small insignificant marginal nodules.

X—December 7, 1932.

Possibly my few aberrant specimens[2] may have been spurious and the results would be strengthened by their elimination. Now I would have no hesitation in discarding a suspicious result provided three or four contrary check experiments were made under similar conditions.

Finally the "geometrical" reaction appears to furnish conclusive evidence even with small numbers because it is impossible that an unknown factor should so reproduce the outline of the incident beam.

The next three points (blank, hypertrophy, atrophy), according to dose, scarcely need further proof or discussion, but some comment may not be out of place. As mentioned above, I will defer the question of specific atrophy or hypertrophy producing frequencies and look at the matter from a broad viewpoint to include both mixed and homogeneous radiations. My work bears out the widely accepted view that if the rate of application of the stimulus is inadequate, a process of repair prevents the occurrence of any visible change. A continued stimulus of higher intensity will produce a biological reaction which appears suddenly at a point termed the threshold dose, a term which is strictly incorrect because it takes no account of time.

The reaction is undoubtedly an expression of repair, a final effort after the perfect process of invisible repair has broken down. In radiotherapy this final effort shows as a vascular change, the X ray erythema and cellular proliferation is not in evidence unless perhaps as a late and obviously secondary change. My work has shown beyond all doubt that a dose of X radiation may lead to the immediate development of hypertrophic and proliferative changes. Pl. IX, Fig. 9, is a beautiful example of hypertrophy which was obtained by means of mixed radiation through intact shell. A similar picture has been obtained in a great many instances by means of homogeneous radiation acting through a shell window, and there was no evidence of any necrosis or degenerative change in such small reactions.

Finally as the disturbance is increased there is a breakdown of tissue structure followed by autolysis giving the picture of atrophy previously described.[2] The atrophic change obtained here by mixed radiation through intact shell is distinct, a fibrous shrunken condition resembling the pseudo atrophy attributed to mixed radiation in my thesis.[1] However, true atrophy has been obtained both by means of mixed radiation and in spurious reactions, but my impression was that of a

secondary nutritional cause. It is possible that there is some distinctive feature in the atrophy obtained by homogeneous rays. Such atrophied reactions have an overhanging hypertrophied margin suggesting a further attempt at repair by ingrowth from the peripheral tissues. The mixed ray pseudo atrophy obtained through intact shell reveals no obvious raised edge but the microscope shows slight peripheral hypertrophy and lymphocyte infiltration.

It is certainly unfortunate that an infective process may cause atrophy or hypertrophy, but after all this is only to be expected as the natural type of response of the tissue. A similar situation occurred in my work with mouse skin,[6] where the insertion of a stitch led to a slight infiltration and epithelial hypertrophy which was of the same general type as the supposed X ray effect.

Microscopically complete atrophy must be identical from any cause because the membrane is completely disorganised and there is nothing to see. It appears obvious that hypertrophic reactions will show differences according to the exciting cause although they may possess certain broad features of similarity. No one will deny the veracity of an X ray erythema, because a poultice may produce a similar appearance. Similarly my work is not concerned with any effect which may be produced in the allantois but with certain changes which may be observed after irradiation.

I ask the reader to accept my first six points, and I hope in later papers to finalise a number of other aspects of my work, commencing with[7] selective action.

As a preliminary to later work I have given a wave length to three figures in the region of the lead and uranium K series, and I hope by this method to obtain some conclusive evidence on the heavy atom theory. Meanwhile there is promise of a new method of investigating the high frequencies by varying the voltage generating mixed radiation. It is interesting to speculate whether this would indicate an exact position or 1·3 V_0 approximately. For example, the maximum action indicated at about 120 KV. may represent the lead K 'evel (87·3 KV.).

There is proof of a variation of action with voltage providing the energy measurement is referred to total incident energy. Previously this was indicated by the variation in threshold dose with different generators.

References.

[1] "An Investigation of the Reaction of Animal Tissues Exposed to Monochromatic X Rays of Different Wave Lengths", thesis aw. M.D., University of Sydney, Feb. 6, 1928. Preliminary notice under same title, *Med. Journ. Aust.*, April 11, 1925.

[2] "The Differential Action of X Rays in Relation to Tissue Growth and Vitality", Part I, *Proc. Roy. Soc.*, B. 105, p. 402.

[3] Ditto, Part II, *Proc. Roy. Soc.*, B. 107, p. 293.

[4] Ditto, Part III, *Proc. Roy. Soc.*, B. 107, p. 302.

[5] Ditto, Part IV, *Proc. Roy. Soc.*, B. 107, p. 308.

[6] "The Reaction of Living Tissues to Homogeneous X Radiation Produced by Crystal Diffraction". (Owing to a misunderstanding, this was not marked Part V as intended.) *Proc. Roy. Soc.*, B. 108, p. 503.

[7] "The Differential Action of X Rays in Relation to Tissue Growth and Vitality", Part VI, *Proc. Roy. Soc.*, B. 110, p. 172.

[8] "A Thermo-electric Instrument for Measuring Total X Ray Energy with a Determination of the Practical Units", *Brit. Journ. Radiol.*, V, N.S., p. 159.

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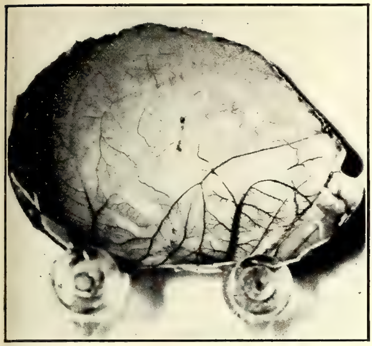
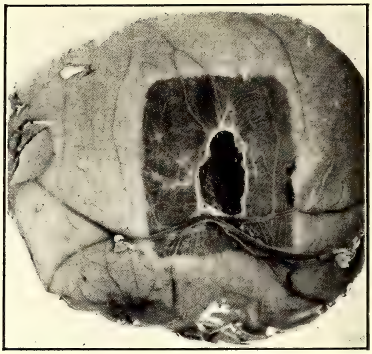


8. Mixed ray reaction through intact shell. Hypertrophy with a pale rectangular area of pseudo-atrophy just at the left. (× ⅔.)



10. Atrophic reaction produced by homogeneous rays, 0·5 Å., in a "window". The geometrical outline of the incident beam is reproduced. (Actual size.)

12. Cross-section of incident mixed ray beam. (Actual size.)

11. Cross-section of incident homogeneous beam. (Actual size.)

9. A hypertrophic reaction produced by mixed radiation acting through intact shell. Normal on the left. (× 15.)

THE CHEMICAL CHANGES INVOLVED IN THE FORMATION OF AMINOAZO COMPOUNDS.

Part II.—ANILINE NITRITE.

By John Campbell Earl, D.Sc., Ph.D.,

and Norman Frederick Hall, B.Sc.

(With one Text-figure.)

(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

In a previous paper (*this Journal*, 1932, **66**, 157) it was suggested that aniline nitrite under the influence of acids might undergo intramolecular change with the formation of a diazo-compound. Since solutions which apparently contain aniline nitrite are produced when equimolecular proportions of sodium nitrite and aniline hydrochloride, in methanol, are mixed, the action of acids on such solutions has now been studied by the dilatometric method previously used. When a weak acid, such as acetic acid, is used, the irregularity in the volume-temperature curve of the reaction-mixture is less abrupt than when hydrochloric acid or pyridine hydrochloride is added. The curves A, B, C, D in the accompanying diagram illustrate this; the data from which they are drawn are given in the experimental part of the paper.

The isolation of aniline nitrite and a study of its behaviour under acid conditions, appeared to us to be desirable and was successfully accomplished. When a cold concentrated aqueous solution of aniline hydrochloride is added to a cold concentrated solution of

sodium nitrite, slightly in excess of an equimolecular proportion, the reaction-mixture becomes almost solid. Ether dissolves out the aniline nitrite, which may be recovered in a white crystalline condition by removal of the solvent under reduced pressure.

As might be expected, aniline nitrite so isolated is an unstable substance. Aqueous solutions of it rapidly deposit a precipitate of diazoaminobenzene and the solid itself becomes yellow at room temperature. It was possible, however, to determine the aniline/nitrous acid

ratio, and so to prove the identity of the substance, by methods which are described later in this paper.

Aniline nitrite when dissolved in methanol undergoes the characteristic volume change under the influence of acids, as is shown by curves E, F and G.

These observations do not necessarily support the conclusion that aniline nitrite undergoes an intramolecular rearrangement when acted upon by acids. The possibility still remains that the reaction involving volume change is that of nitrous acid or methyl nitrite with a salt of aniline. Studies on the behaviour of methylaniline nitrite have been instituted, since in this case the final product, the nitrosamine, is stable and the possible complications due to the formation, in the case of aniline nitrite, of diazoaminobenzene, are avoided. The results of these studies will be given in a subsequent paper.

Experimental.

Preparation of Aniline Nitrite.

A concentrated solution of sodium nitrite (1·5 grams in 3 cc. of water) was placed in a small flask, covered with a layer of pure ether (20 cc.) and cooled to about –15° C. At the same time a solution of pure aniline hydrochloride (2 grams in 5 cc. of water) was prepared and cooled to –8° C, lower temperatures in this case causing formation of crystals. The distilled water used in the preparation of the solutions was boiled and cooled rapidly immediately before use to expel carbon dioxide. In the initial experiments equimolecular proportions of sodium nitrite and aniline hydrochloride were used, but it was found that, owing to the difficulty of instantaneous mixing, some decomposition occurred; this was

Tabular Summary of Data relating to Volume-Temperature Curves.

Curve	X	Y	Z	R	H	S	T
A	Aniline HClde 0·203	Sodium nitrite 0·203	Acetic acid 1·3	1 : 1 : 7	0·05	5·0	7·8
B	Aniline HClde 0·203	Sodium nitrite 0·203	Acetic acid 4·0	1 : 1 : 20	0·05	4·0	7·0
C	Aniline HClde 0·182	Sodium nitrite 0·182	Pyridine HClde ca 0·2	1 : 1 : 1	0·05	4·0	8·1
D	Aniline HClde 0·183	Sodium nitrite 0·183	Hydrochloric acid 0·091	1 : 1 : 0·5	0·05	4·0	7·6
E	Aniline nitrite ca 0·4	—	Acetic acid 0·83	—	0·05	4·0	8·4
F	Aniline nitrite ca 0·3	—	Hydrochloric acid 0·09	—	0·05	5·0	7·0
G	Aniline nitrite ca 0·3	—	Aniline HClde 0·4	—	0·05	4·0	8·4

X, Y, Z = Concentration of reactants—Mols per litre.
R = Molar ratio—X : Y : Z.
H = Rate of temperature rise throughout—Degrees Centigrade per minute.
S = Time interval between mixing and first reading—Minutes.
T = Temperature of first reading—Degrees Centigrade.

minimised by using a considerable excess of nitrite (up to 1·5 mols) and making the nitrite solution faintly alkaline to litmus. Very concentrated solutions of the reactants are advisable since an excess of water favours the rapid precipitation of diazoaminobenzene.

The aniline hydrochloride solution was poured rapidly into the nitrite solution with vigorous stirring, care being taken that none of the former touched the sides of the flask. A white precipitate formed almost immediately and on further stirring dissolved in the ether layer. The ethereal solution was decanted into a large test-tube containing anhydrous sodium sulphate and cooled to –15° C. The extraction with ether was repeated.

After the ethereal solution had been allowed to dry for a few minutes, it was decanted into a small filter flask fitted with a capillary tube (to admit a fine stream of air, previously cooled and dried) and the ether removed under reduced pressure. After a period of from twenty to sixty minutes, a mass of white needles, soluble in water, ether or alcohol, remained.

Owing to the instability of the substance, it was difficult to determine the actual yield, but it approximated to sixty per cent. in those cases in which the product was isolated for analysis. In such cases a maximum yield was sacrificed because rapidity of working was essential for the obtaining of a pure product.

Analysis of Aniline Nitrite.

The white product obtained by working as rapidly as possible showed only a slight yellow tinge at the edges. To such a product, immediately after the removal of the ether, a ten per cent. aqueous solution of pure sodium hydroxide cooled to –15° C. was added with vigorous

stirring. Decomposition into aniline and sodium nitrite took place at once. The aniline was carefully distilled off in a current of steam, the distillate being mixed with pure hydrochloric acid and made up to a known volume. The aniline was estimated volumetrically in a portion of this solution by adding a known volume of N/10 bromide-bromate solution together with potassium iodide, the liberated iodine being titrated with standard thiosulphate.

The alkaline solution of sodium nitrite remaining after the steam distillation was made up to standard volume and the nitrite estimated by Busvold's modification (*Chem. Zeitung*, 1915, **39**, 214) of Raschig's method (*Berichte*, 1905, **38**, 3911).

By this means the quantities of nitrous acid and aniline combined together in the original material were found to be:

Nitrous acid	0·453 gram
Aniline	0·877 gram

The quantity of aniline nitrite taken for the analysis was, therefore, 1·330 grams, the calculated composition of which would be:

Nitrous acid	0·446 gram
Aniline	0·884 gram

It will be noticed that the analytical results indicate a content of nitrous acid slightly lower than that calculated; this is readily understandable in view of the extreme case with which diazoaminobenzene is formed with the consequent loss of nitrous acid.

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DERIVATIVES OF 2-PHENYL-QUINOLINE.

Part II.

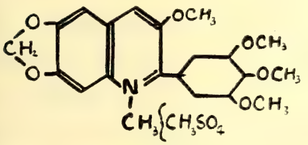
SOME "ATOPHANS" WITH SUBSTITUENT BASIC GROUPS.

By Muriel Gertrude Holdsworth, M.Sc.,

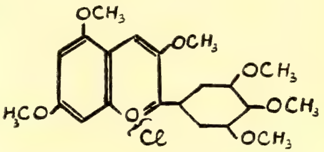
and Francis Lions, B.Sc., Ph.D.

(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

It was noted by Pratt and Robinson (*Journ. Chem. Soc.* (1925), **127**, 173) on comparing the methosulphate of 3-methoxy-6:7-methylene dioxy-2-(3′:4′:5′-trimethoxyphenyl)-quinoline (A) with delphinidin chloride hexamethyl ether (B), in which the auxiliary valencies of the nitrogen and oxygen respectively are saturated, that the quinolinium and benzopyrylium nuclei function quite differently as chromophores, the former substance being orange whilst the latter is reddish violet with a green lustre.



(A)



(B)

Pratt and Robinson remarked:

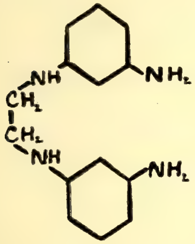
"It may well be that the methoxyl groups are able to decentralise the cationic valency of the pyrylium nucleus and so produce changes of orbits of electrons owing to recurrent redistribution of the charge, whilst, on the other hand, the powerfully basic quinolinium nucleus is able to ignore the claims of the weak auxochromes. We are thus led to anticipate that the aminophenyl quinolinium salts will resemble tinctorially the hydroxyphenyl benzopyrylium salts and it is hoped that an experimental test of this point will be made."

Moir (*Trans. Roy. Soc. South Africa* (1928), **16**, 121) has shown, however, that the polyamino-2-phenyl quinolines examined by him are not so intensely coloured as the corresponding flavylium compounds, though he commented on the noticeable deepening of colour with the introduction of a dimethylamino-group in certain positions.

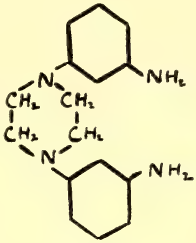
The comparison of phenylquinolinium alkyl salts containing amino or substituted amino groups with the corresponding related hydroxyl substituted flavylium salts is of very considerable interest and the authors are at present engaged in an extensive research on this subject. In the present paper there are described some "atophans"—derivatives of 2-phenyl-quinoline-4-carboxylic acid—which have substituent amino groups. The decarboxylation of these to the corresponding substituted 2-phenyl-quinolines and the tinctorial properties of these latter, will be communicated in a later paper.

Comparatively few derivatives of 2-phenylquinoline-4-carboxylic acid containing one or more amino or substituted amino groups, have so far been described. In the present communication there are described, (*a*) the preparation of certain "atophans" containing a dimethylamino group in the 7-position in the quinoline nucleus, by the condensation of m-dimethylamino aniline with various aldehydes and pyruvic acid in alcoholic solution; (*b*) the preparation of several derivatives of m-phenanthroline by condensation of m-phenylenediamine with aromatic aldehydes and pyruvic acid in alcoholic solution; and (*c*) the preparation of certain quinoline derivatives having two quinoline nuclei by the condensation of sym-di-m-aminophenylamino ethane (C) and of 1:4-di-(m-aminophenyl)-piperazine (D) with certain

aromatic aldehydes and pyruvic acid in alcoholic solution.



(C)



(D)

The colours of the substances obtained range from yellowish brown to deep red. The colours of their acid solutions are particularly intense and striking.

The nomenclature of the compounds described is made clear by reference to the numbered skeleton diagrams (Figures I, II, and III).

Experimental.

7-Hydroxy-2-(4′-dimethylaminophenyl)-quinoline-4-carboxylic acid (I).

A solution of m-aminophenol (3 g.) in alcohol (50 cc.) was added gradually to a solution of p-dimethylamino-benzaldehyde (5 g.) and pyruvic acid (3 g.) in boiling alcohol (100 cc.). After boiling for a few minutes the cinchoninic acid commenced to precipitate, as a red powder. After refluxing for one hour the solution was cooled and filtered.

As it is insoluble in ordinary organic solvents this substance was purified for analysis by solution in potassium carbonate solution, and treatment of the hot solution with "Norite" followed by filtration and acidification of the filtrate with acetic acid. After washing with water and drying, the purified substance did not melt below 300° C.

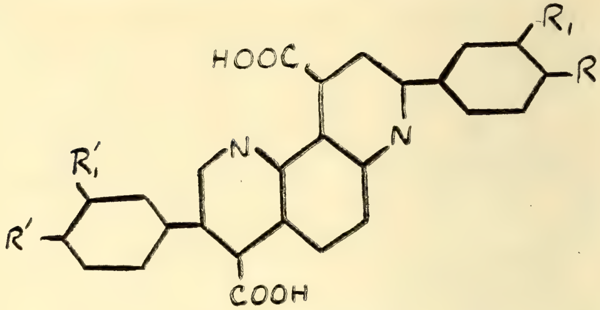


Fig I.

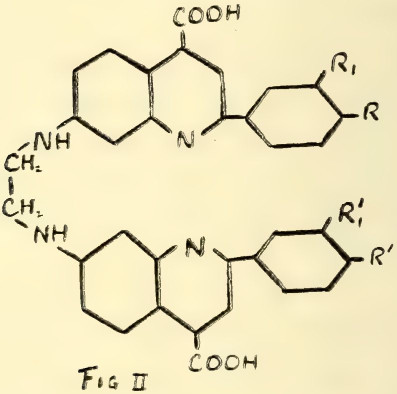


Fig II

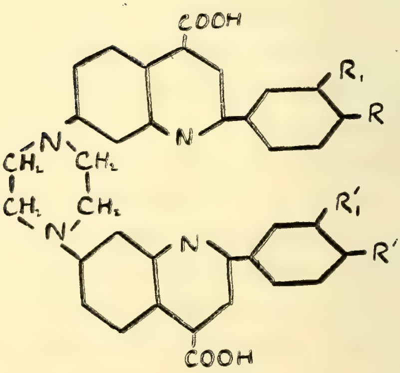


Fig III

Found C = 69·8, H = 5·1%; calculated for $C_{18}H_{16}O_3N_2$, C = 70·1, H = 5·2%.

Treatment of the acid with aqueous ammonia gave a brown solution. It was also soluble in dilute sodium hydroxide solution forming a yellow solution. The yellow Ba-salt was moderately soluble. Mg-salt was orange-yellow and insoluble. Al-salt insoluble and red. Pb-salt yellow and insoluble. Addition of hydrochloric acid to the solution of the acid in ammonia gave a red precipitate.

7-Dimethylamino-2-(4′-methoxyphenyl)-quinoline-4-carboxylic acid (II).

Heating under reflux of a solution of m-dimethylamino-aniline (5 g.), anisaldehyde (5 g.) and pyruvic acid (3·5 g.) in alcohol (80 cc.) for 15 minutes led to formation of this cinchoninic acid which was precipitated in deep orange coloured needles (4 g.). It could be recrystallised from hot glacial acetic acid and was thus purified. The melting point is approximately 315° C.

Found C = 70·7, H = 5·8%; calculated for $C_{19}H_{18}O_3N_2$, C = 70·8, H = 5·6%.

The acid was soluble in ammonia, forming a yellow solution. On heating the colour became orange and eventually a crystalline precipitate came down. The yellow sodium salt was soluble in water, but the Mg, Ba, Al and Pb salts were all insoluble. The first two were yellow amorphous solids, the third was red, and the Pb salt was orange yellow. From the ammoniacal solution of the acid hydrochloric acid produced a deep red precipitate.

7-Dimethylamino-2-(3′:4′-methylenedioxyphenyl)-quinoline-4-carboxylic (III).

This substance was readily obtained as a precipitated orange powder (3 g.) when a solution of m-dimethyl-aminoaniline (5 g.), piperonal (5 g.), and pyruvic acid (3·5 g.) in alcohol (80 cc.) was refluxed for fifteen minutes and then cooled. It could be recrystallised from glacial acetic acid and did not melt below 300° C.

Found C = 68·2, H = 5·3%; calculated for $C_{19}H_{16}O_4N_2$, C = 67·9, H = 4·8%.

The acid was soluble in aqueous ammonia to a yellow solution with a distinct yellow green fluorescence. On standing a yellow NH_4-salt crystallised out. If the solution were heated it became red in colour. The Na-salt was yellow and crystalline and dissolved in hot water readily. The Mg-, Ba-, and Pb-salts were all obtained as orange coloured crystalline insoluble precipitates. The Al-salt was also crystalline and insoluble, but was of a red-gold colour. Addition of hydrochloric acid to the solution of the acid in ammonia gave a deep red precipitate.

7-Dimethylamino-2-(4′-dimethylamino-phenyl)-quinoline-4-carboxylic acid (IV).

This cinchoninic acid was precipitated as a dark red powder (4 g.) from a boiling solution of m-dimethylaminoaniline (5 g.), p-dimethylaminobenzaldehyde (6 g.) and pyruvic acid (3·5 g.) in alcohol (80 cc.) after fifteen minutes. It also could be recrystallised from glacial acetic acid and did not melt below 300°.

Found C = 71·6, H = 6·7%; calculated for $C_{20}H_{21}O_2N_3$, C = 71·6, H = 6·3%.

The acid dissolved in dilute aqueous ammonia solution to a reddish-brown solution. The Na-salt was yellow and only sparingly soluble in cold water. The Mg- and Ba-salts were both bright red and insoluble. The Al-salt was a crystalline crimson precipitate. The Pb-salt was a brick-red insoluble powder. Hydrochloric acid precipitated a purple precipitate from the solution in ammonia.

α-α'-Dianisyl-m-phenanthroline-γ-γ'-dicarboxylic acid (V).

(Fig. I, R, $R^1 = OCH_3$; R_1, R_1^1 = H.)

A solution of m-phenylene diamine (5 g.), anisaldehyde (11 g.) and pyruvic acid (8 g.) in alcohol (150 cc.) was heated under reflux for 45 minutes. A heavy dark oil gradually separated. On cooling it solidified to a brownish-red powder (17 g.). After several recrystallisations from alcohol it melted at 210°.

Found C = 69·6, H = 4·4%; calculated for $C_{28}H_{20}O_6N_2$, C = 70·0, H = 4·2%.

This substance did not dissolve very easily in ammonia. The solution obtained was brownish-red in colour. The Na-, Mg- and Ba-salts were all sparingly soluble and yellow. The Al-salt was orange in colour and insoluble, whilst the Pb-salt formed a heavy yellow insoluble powder. With hydrochloric acid the ammoniacal solution yielded a red insoluble precipitate.

$\alpha:\alpha'$-Dipiperonyl-m-phenanthroline-$\gamma:\gamma'$-dicarboxylic acid (VI).

(Fig. I, RR_1, $R^1R_1^1$ = $:O_2CH_2$.)

This acid was precipitated as a dark red powder (16 g.) after heating a solution of m-phenylene diamine (5 g.), piperonal (14 g.) and pyruvic acid (8 g.) in alcohol (150 cc.) under reflux for one hour. After recrystallisation from alcohol it was obtained in minute dark red prisms which melted at 205-206°.

Found C = 66·1, H = 3·2%; calculated for $C_{28}H_{16}O_8N_2$, C = 66·1, H = 3·1%.

The ammonium salt of this acid was moderately soluble in water, forming a brownish red solution. The Na-, Ba- and Pb-salts were yellow sparingly soluble powders. The Mg-salt was yellowish brown and insoluble, whilst the insoluble Al-salt was red. Hydrochloric acid precipitated a deep red solid from the ammoniacal solution.

$\alpha:\alpha'$-Di-(p-dimethylaminophenyl)-m-phenanthroline-$\gamma:\gamma'$-dicarboxylic acid (VII).

(Fig. I, R, R^1 = $N(CH_3)_2$; R_1, R_1^1 = H.)

This derivative of m-phenanthroline was precipitated as a dark red oil (17 g.) when a solution of m-phenylene diamine (5 g.), p-dimethylaminobenzaldehyde (14 g.) and pyruvic acid (8 g.) in alcohol (150 cc.) was refluxed for one hour. On cooling the oil crystallised, and after recrystallisation from boiling alcohol very dark red minute crystals melting at 234° were obtained.

Found C = 70·7, H = 5·6%. Calculated for $C_{30}H_{26}O_4N_4$, C = 71·1, H = 5·1%.

The sparingly soluble ammonium salt of this acid dissolved in water to a brownish-red solution. The yellow Na-salt was sparingly soluble in cold water but moderately soluble in hot. The Ba-salt which was orange in colour was moderately soluble. The Mg- and Pb-salts formed orange-yellow insoluble powders. The insoluble Al-salt was red; whilst hydrochloric acid gave a deep-red precipitate from the ammoniacal solution.

Sym-bis-(2-phenyl-4-carboxy-7-quinolylamino)-ethane (VIII).

(Fig. II, R, R^1, R_1, R_1^1 = H.)

Sym-bis-(m-aminophenylamino) ethane was prepared by reduction of the corresponding nitro compound, which

in turn was prepared from ethylene dibromide, m-nitraniline and anhydrous potassium carbonate, according to the method of Borsche and Camper Titsingh (*Ber.* (1907), **40**, 5014). By refluxing a solution of this base (8 g.), benzaldehyde (7 g.) and pyruvic acid (6 g.) in alcohol (100 cc.) for fifteen minutes condensation appeared to occur readily and the quinoline derivative was precipitated almost immediately as a light brown powder (10 g.). It was very sparingly soluble in the usual organic solvents but could be purified by solution in hot aniline, cooling, and addition of dry ether which caused it to be precipitated; or by recrystallisation from much glacial acetic acid. When pure it formed fine brown needles melting at 280° (decomp.).

Found C = 73·4, H = 5·3%; calculated for $C_{34}H_{26}O_4N_4$, C = 73·6, H = 4·7%.

The ammonium salt dissolved in water to a brown solution. The Na-, Mg-, Ba- and Pb-salts formed light yellow sparingly soluble precipitates. The Al-salt was orange and insoluble. Hydrochloric acid precipitated a deep-red solid from the solution of the ammonium salt.

Sym-bis-(2-Anisyl-4-carboxy-7-quinolylamino)-ethane (IX).

(Fig. II, R, R^1 = OCH_3; R_1, R_1^1 = H.)

A solution of sym-bis-(m-aminophenylamino)-ethane (8 g.), anisaldehyde (7 g.) and pyruvic acid (6 g.) in alcohol (100 cc.) was gently refluxed for fifteen minutes. Condensation occurred immediately and the quinoline derivative was precipitated as a brown powder (8·5 g.). Insoluble in the usual organic solvents it was purified in the same way as described for the previous substance —solution in aniline and reprecipitation with dry ether. It melted at 276°.

Found C = 69·9, H = 5·5%; calculated for $C_{36}H_{30}O_6N_4$, C = 70·4, H = 4·9%.

The NH_4-salt was brown and sparingly soluble. The Na-, Mg-, Ba- and Pb-salts were only very sparingly soluble and yellowish brown in colour. The insoluble Al-salt was orange-red. Hydrochloric acid precipitated a deep-red solid from the solution of the NH_4-salt.

Sym-bis-(2-veratryl-4-carboxy-7-quinolylamino)-ethane (X).

(Fig. II, R, R^1, R_1, R_1^1 = OCH_3.)

This substance (10·5 g.) was obtained and purified in a similar manner to the previous two substances from a hot solution of sym-bis-(m-aminophenylamino)-ethane (8 g.), veratric aldehyde (11 g.) and pyruvic acid (6 g.) in alcohol (100 cc.). It formed a light brown powder melting at 264°.

Found C = 66·9, H = 5·2%; calculated for $C_{38}H_{34}O_8N_4$, C = 67·6, H = 5·0%.

The NH_4-salt was moderately soluble in water to a brownish-red solution. The Na-, Mg- and Ba-salts were all yellow and but sparingly soluble. The insoluble Pb-salt was orange yellow, the insoluble Al-salt, orange-red. Hydrochloric acid precipitated a deep-red solid from the aqueous solution of the ammonium salt.

Sym-bis-(2-piperonyl-4-carboxy-7-quinolylamino)-ethane (XI).

(Fig. II, R, R_1, R^1 R_1^1 = $:O_2CH_2$.)

Obtained as a brown powder (11 g.) from a hot solution of sym-bis-(m-aminophenylamino)-ethane (8 g.), piperonal (11 g.) and pyruvic acid (6 g.) in alcohol (100 cc.) and purified in the usual way from aniline solution this substance melted at 290°.

Found C = 66·9, H = 4·6%; calculated for $C_{36}H_{26}O_8N_4$, C = 67·3, H = 4·1%.

The moderately soluble NH_4-salt formed a brown solution in water. The Na-, Mg-, Ba- and Pb-salts were all sparingly soluble and light yellow in colour. The insoluble Al-salt was orange-red. Hydrochloric acid gave a deep-red precipitate with the solution of the ammonium salt.

Sym-bis (2-vanillyl-4-carboxy-7-quinolylamino)-ethane (XII).

(Fig. II, R, R^1 = OH; R_1, R_1^1 = OCH_3.)

This substance was obtained as a light reddish-brown powder (11 g.) from a hot alcoholic solution of vanillin

(10 g.), sym-bis-(m-aminophenylamino)-ethane (8 g.) and pyruvic acid (6 g.), and was purified from aniline solution as above. It melted at 256°.

Found C = 66·5, H = 5·0%; calculated for $C_{36}H_{30}O_8N_4$, C = 66·9, H = 4·6%.

The ammonium salt of this acid dissolved readily in water to a dark red-brown solution. The Na-salt was red-brown and soluble. The Mg-, Ba- and Pb-salts were all sparingly soluble and yellowish brown. The Al-salt was orange yellow and insoluble. Hydrochloric acid gave a deep-red precipitate from the solution of the ammonium salt.

Sym-bis-(2-p-dimethylaminophenyl-4-carboxy-7-quinolylamino)-ethane (XIII).

(Fig. II, R, R^1 = $N(CH_3)_2$; R_1, R_1^1 = H.)

Obtained from a hot solution of sym-bis-(m-aminophenylamino)-ethane (8 g.), p-dimethylaminobenzaldehyde (10 g.) and pyruvic acid (6 g.) in alcohol (100 cc.) as a dark red powder (12 g.) this compound after purification in the usual way melted at 260°.

Found C = 70·9, H = 6·0%; calculated for $C_{38}H_{36}O_4N_6$, C = 71·2, H = 5·6%.

The ammonium salt was moderately soluble, the solution being red-brown. The Na- and Mg-salts were light yellow in colour and sparingly soluble. The Ba- and Pb-salts were insoluble and yellowish brown in colour. The insoluble Al-salt was bright orange-red. Hydrochloric acid produced an intense purple precipitate from the solution of the ammonium salt.

1:4-Di-(m-aminophenyl)-piperazine.

This base was obtained by reduction with tin and hydrochloric acid of the 1:4-di-(m-nitrophenyl)-piperazine previously described by Borsche and Camper Titsingh (*Ber.* (1907), **40**, 5014) who prepared this latter substance by refluxing together m-nitroaniline and ethylene dibromide in presence of anhydrous sodium acetate. We found it more advantageous to use anhydrous potassium carbonate, and the method adopted was as follows: Pure m-nitroaniline (130 g.) and dry potassium carbonate (300 g.) were finely powdered and

intimately mixed, and after addition of ethylene dibromide (188 g.) heated in a reflux apparatus in an oil-bath maintained at 150° for three hours. After cooling, the product was treated with water to remove potassium salts, and then with alcohol to remove any unchanged m-nitroaniline. Finally, after washing with a little acetone, the orange product was recrystallised from hot aniline, and obtained in orange prisms melting at 206° (*cf.* Borsche and Titsingh, *loc. cit.*).

Treatment of this 1:4-di-m-nitrophenyl piperazine (25 g.) with metallic tin (35 g.) and concentrated hydrochloric acid (100 cc.) at 100° until all the tin had dissolved gave a clear solution from which addition of further concentrated hydrochloric acid (100 cc.) and cooling produced a white precipitate, which was collected and dissolved in water. Addition of sodium hydroxide solution in excess to the filtered aqueous solution produced a greyish white precipitate of the crude base. Recrystallised several times from benzene it was obtained in white leaflets melting at 102°.

Found C = 71·2, H = 7·7%; calculated for $C_{16}H_{20}N_4$, C = 71·6, H = 7·5%.

Condensation of this base with aldehydes and pyruvic acid by warming for a few minutes in alcoholic solution, to the corresponding di-quinolyl piperazine derivatives could be effected with great ease, a precipitate forming almost at once. The method adopted for purification of all these substances was the same as that for the diquinolylamino ethane derivatives previously described, *viz.*, solution in hot aniline, cooling and then precipitation with dry ether, followed by washing several times with ether.

1:4-Di-(2-phenyl-4-carboxy-7-quinolyl)-piperazine (XIV).

(Fig. III, R, R_1, R^1, R_1^1 = H.)

A light brown powder (3·5 g.) was obtained from 1:4-di-(m-aminophenyl)-piperazine (3 g.), benzaldehyde (2 g.) and pyruvic acid (2 g.) in alcohol (80 cc.) which after purification melted at 265°.

Found C = 74·2, H = 5·3%; calculated for $C_{36}H_{28}O_4N_4$, C = 74·5, H = 4·8%.

The ammonium salt was moderately soluble in water to a brown solution. The Na- and Ba-salts were sparingly soluble and yellow in colour. The insoluble Al-salt was orange-red and the insoluble Mg- and Pb-salts were yellowish brown. Hydrochloric acid gave a deep-red precipitate with the solution of the ammonium salt.

1:4-Di-(2-anisyl-4-carboxy-7-quinolyl)-piperazine (XV).

(Fig. III, R, R_1 = OCH_3; R_1, R_1^1 = H.)

A light reddish brown powder (4 g.) was obtained from a solution of 1:4-di-(m-aminophenyl)-piperazine (3 g.), anisaldehyde (3 g.) and pyruvic acid (2 g.) in alcohol (80 cc.) after heating for a few minutes, which after purification melted at 217°.

Found C = 71·1, H = 5·4%; calculated for $C_{38}H_{32}O_6N_4$, C = 71·3, H = 5·0%.

The ammonium salt was but sparingly soluble in hot water, giving a yellowish brown solution. The sparingly soluble Na-salt was yellow. The Mg-, Ba- and Pb-salts were insoluble and yellowish brown in colour. The insoluble Al-salt was red. Hydrochloric acid gave a deep-red precipitate with the aqueous solution of the ammonium salt.

1:4-Di-(2-veratryl-4-carboxy-7-quinolyl)-piperazine (XVI).

(Fig. III, R, R_1, R^1, R_1^1 = OCH_3.)

This substance was obtained as a brown powder (3·5 g.) by refluxing a solution of 1:4-di-(m-aminophenyl)-piperazine (3 g.), veratric aldehyde (3·5 g.) and pyruvic acid (2 g.) in alcohol (80 cc.) for fifteen minutes. After purification it melted at 242°.

Found C = 68·4, H = 5·6%; calculated for $C_{40}H_{36}O_8N_4$, C = 68·6, H = 5·1%.

The yellowish NH_4-salt was soluble to some extent in hot water, forming a reddish brown solution. The Na-salt was yellow and sparingly soluble. The Ba-, Mg- and Pb-salts were all yellowish-brown and insoluble. The insoluble Al-salt was red. Hydrochloric acid precipitated a deep-red powder from the aqueous solution of the ammonium salt.

1:4-Di-(2-piperonyl-4-carboxy-7-quinolyl)-piperazine (XVII).

(Fig. III, RR_1, R^1, R_1^1 = $:O_2CH_2$.)

A light brown powder (3 g.) was obtained by refluxing an alcoholic solution of 1:4-di-(m-aminophenyl)-piperazine (3 g.), piperonal (3·5 g.) and pyruvic acid (2 g.) for a few minutes. After purification it melted at 236°.

Found C = 67·9, H = 4·6%; calculated for $C_{38}H_{28}O_8N_4$, C = 68·3, H = 4·2%.

The NH_4-salt was sparingly soluble and gave a red-brown solution. The Na-salt was yellow. The Mg- and Ba-salts were yellowish brown and insoluble. The Al-salt was orange red and the Pb-salt orange in colour, both being insoluble. Hydrochloric acid precipitated a deep-red solid from the aqueous solution of the ammonium salt.

1:4-Di-(2-vanillyl-4-carboxy-7-quinolyl)-piperazine (XVIII).

(Fig. III, R, R^1 = OH; R_1, R_1^1 = OCH_3.)

This substance was obtained as a light reddish-brown powder (3 g.) by refluxing an alcoholic solution of 1:4-di-(aminophenyl)-piperazine (3 g.), vanillin (2·5 g.) and pyruvic acid (2 g.) for a few minutes. After purification it melted at 242°.

Found C = 67·6, H = 4·6%; calculated for $C_{38}H_{32}O_8N_4$, C = 67·9, H = 4·8%.

The NH_4-salt was easily soluble in the hot, giving a deep brown solution. The Na-salt was also brown and easily soluble. The Ba- and Mg-salts were insoluble and yellowish brown. The Al-salt was insoluble and brick red in colour. The insoluble Pb-salt was brownish-red in colour. Hydrochloric acid produced a deep-red precipitate from the aqueous solutions of either the NH_4- or Na-salts.

1:4-Di-(2-p-dimethylaminophenyl-4-carboxy-7-quinolyl)-piperazine (XIX).

(Fig. III, R, R^1 = $N(CH_3)_2$; R_1, R_1^1 = H.)

This substance was obtained readily as a deep-red powder (5 g.) by refluxing an alcoholic solution of 1:4-di-(m-aminophenyl)-piperazine (3 g.), p-dimethylaminobenzaldehyde (3 g.) and pyruvic acid (2 g.). After purification it melted at 278°.

Found C = 71·8, H = 6·2%; calculated for $C_{40}H_{38}O_4N_6$, C = 72·1, H = 5·7%.

The NH_4-salt dissolved in hot water forming a deep-red brown solution. The Na-, Ba- and Mg-salts were all sparingly soluble and yellowish brown. The Pb-salt was insoluble and reddish brown in colour. The scarlet Al-salt was also insoluble. Hydrochloric acid produced an intensely coloured reddish purple precipitate from the aqueous solution of the ammonium salt.

A small quantity of each of the quinoline derivatives described above was dissolved in cold concentrated sulphuric acid and the colour noted. The solution was then poured into ice-water and the colour again observed. Usually a remarkable development of colour occurred, particularly with those derivatives having several substituent basic groups. It is worthy of comment that the treatment did not apparently remove the methylene dioxy group from those derivatives in which it was contained. The results obtained are tabulated below.

Substance.	Colour in concentrated sulphuric acid.	Colour after dilution.
I	Brownish yellow	Intense red
II	Orange	Intense magenta
III	Deep-red	,, ,,
IV	Yellow	Deep purple
V	Reddish brown	Red brown precipitate
VI	Deep red	Red precipitate
VII	Deep red brown	Deep red
VIII	Brownish yellow	Light reddish brown precipitate
IX	Brownish red	Brownish red precipitate
X	,, ,,	,, ,, ,,
XI	,, ,,	,, ,, ,,
XII	,, ,,	,, ,, ,,
XIII	,, ,,	Deep red solution
XIV	Deep red brown	Red precipitate
XV	,, ,, ,,	,, ,,
XVI	,, ,, ,,	,, ,,
XVII	,, ,, ,,	,, ,,
XVIII	,, ,, ,,	,, ,,
XIX	Brownish yellow	Deep red solution

Department of Organic Chemistry,
The University of Sydney.

DERIVATIVES OF 2-PHENYL QUINOLINE.

PART III.

SOME DERIVATIVES OF POLYHYDROXY "ATOPHANS".

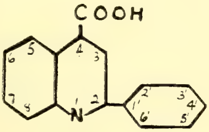
By MURIEL GERTRUDE HOLDSWORTH, M.Sc.,

and FRANCIS LIONS, B.Sc., Ph.D.

(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

Many derivatives of 2-phenyl quinoline-4-carboxylic acid ("Atophan") are known in which there are substituent phenolic hydroxyl groups or phenolic ether groups. Theoretical considerations show that there may be 8 isomeric monohydroxylated 2-phenyl quinoline-4-carboxylic acids, and no less than thirty-one dihydroxy isomers. (When the number of hydroxyl groups is larger the number of possible isomers also increases.) In the present paper are briefly described a few derivatives of 2-phenyl quinoline-4-carboxylic acid which have been obtained during application of the Döbner synthesis and the Pfitzinger synthesis to the preparation of 2-phenyl quinoline-4-carboxylic acid derivatives. The decarboxylation of these substances and the tinctorial properties of the resultant 2-phenyl quinoline derivatives will be described in a later paper.

The nomenclature of the compounds described is made clear by reference to the following numbered skeleton diagram:



Experimental.

2-(3′:4′-Dihydroxyphenyl)-quinoline-4-carboxylic acid.

A solution of aniline (3 g.) in alcohol (20 cc.) was added gradually to a solution of pyruvic acid (3 g.) and protocatechuic aldehyde (5 g.) in boiling alcohol (50 cc.). After about thirty minutes' heating under reflux a brownish yellow powder commenced to crystallise. Heating was continued for a further thirty minutes, after which the solution was cooled and filtered. The precipitated cinchoninic acid was found to be practically insoluble in all the usual organic solvents. It was purified by solution in concentrated potassium carbonate solution and treatment of the resultant dark red solution in the hot with animal charcoal followed by filtration and treatment of the filtrate with dilute acetic acid. After careful washing and drying the purified orange-yellow acid did not melt below 300°.

Found C = 68·0, H = 4·2%; calculated for $C_{16}H_{11}O_4N$, C = 68·3, H = 3·9%.

The NH_4-, Na-, and Mg-salts of this substance are all readily soluble to deep red solutions in water. The Ba-salt is also red-brown in colour and is somewhat soluble. The insoluble Al-salt was deep red in colour, and the insoluble Pb-salt brick red. Hydrochloric acid produces a brick red precipitate from a solution of the alkali salts. The acid dissolved readily in cold concentrated sulphuric acid from which water precipitated an orange red solid.

7-hydroxy-2-(2′-hydroxyphenyl)-quinoline-4-carboxylic Acid.

Heating of a solution of m-aminophenol (3 g.), salicylaldehyde (3·5 g.) and pyruvic acid (2·5 g.) in alcohol (100 cc.) under reflux for some time led to formation of the expected quinoline derivative, though only in poor yield (1 g.). It was obtained as a yellow powder, insoluble in the usual organic solvents and was purified by solution in potassium carbonate solution, heat treatment with animal charcoal and reprecipitation

with dilute acetic acid as before. The purified substance did not melt below 300°.

Found C = 68·4, H = 4·1%; calculated for $C_{16}H_{11}O_4N$, C = 68·3, H = 3·9%.

The NH_4-, Na-, Mg-, and Ba-salts of this acid are all soluble in water, forming red-brown solutions. The Al- and Pb-salts are insoluble and yellow. Hydrochloric acid gives a yellow precipitate from the aqueous solutions of the alkali salts. The acid dissolved in cold concentrated sulphuric acid to give an orange red solution from which addition of water gave a light yellow precipitate.

2-(2′-hydroxy-3′:4′-dimethoxyphenyl)-quinoline-4-carboxylic Acid.

This substance was obtained by an application of Pfitzinger's synthesis. To a solution of isatin (10 g.) in 30% potassium hydroxide (60 cc.) was added 2-hydroxy-3:4-dimethoxyacetophenone (12 g.), and the solution was heated at 100° for 8 hours. After dilution with water (200 cc.) the solution was boiled with animal charcoal and the quinoline derivative (12 g.) recovered from the filtrate with dilute acetic acid. Recrystallised from alcohol, it was obtained in reddish brown needles melting at 245°.

Found C = 66·3, H = 5·0%; calculated for $C_{18}H_{15}O_5N$, C = 66·5, H = 4·6%.

This quinoline acid dissolves readily in aqueous ammonia or alkali solutions giving yellow solutions. The Mg-, Al-, and Pb-salts are insoluble and yelow, and the insoluble Ba-salt is orange yellow. Hydrochloric acid produces a yellow precipitate from solutions of the alkali salts. The solution of the acid in cold concentrated sulphuric acid was brownish yellow in colour. Addition of water caused the precipitation of yellow solid.

2-(2′:3′:4′-Trimethoxyphenyl)-quinoline-4-carboxylic Acid.

A solution of isatin (10 g.) and 2:3:4-trimethoxyacetophenone (15 g.) in 30% alcoholic potassium hydroxide solution (70 cc.) was heated under reflux for ten hours. The alcohol was then distilled off and after addition of water the solution was heated with animal

charcoal and filtered. By acidification of the filtrate with acetic acid the quinoline derivative (13 g.) crystallised and was filtered off. Recrystallised from alcohol it was obtained in pale yellow needles melting at 196°.

Found C = 67·0, H = 5·3%; calculated for $C_{19}H_{17}O_5N$, C = 67·2, H = 5·0%.

The NH_4-salt was yellow and soluble. The very pale yellow Na-salt was only moderately soluble. The Mg- and Ba-salts were insoluble in water and cream-coloured. The insoluble Al-salt was lemon-yellow and the insoluble Pb-salt was almost white. Hydrochloric acid produced a yellow precipitate from a solution of the ammonium salt. The acid dissolved in cold concentrated sulphuric acid to an orange solution. This became yellow in colour on dilution, and after standing for some time a yellow precipitate formed.

7-Hydroxy-2-(3′:4′-dihydroxyphenyl)-quinoline-4-carboxylic Acid.

Refluxing for a few minutes of a solution of m-aminophenol (5 g.), protocatechuic aldehyde (5 g.) and pyruvic acid (4 g.) in alcohol (100 cc.) led to rapid formation of the trihydroxyatophan, which was precipitated as a light brown powder (4·5 g.). It was purified by solution in aqueous potassium carbonate solution, heat treatment with animal charcoal, filtration and acidification of the filtrate with dilute acetic acid as before and was thus obtained as a light brown powder which did not melt below 300°.

Found C = 64·2, H = 4·0%; calculated for $C_{16}H_{11}O_5N$, C = 64·6, H = 3·7%.

The NH_4-, Na- and Ba-salts of this acid were all soluble, dissolving in water to dark red solutions. The insoluble Mg-salt was red-brown, and Pb-salt was insoluble and red, and the insoluble Al-salt was deep red in colour. Hydrochloric acid produced a red precipitate from the solution of the acid in dilute ammonia. The acid dissolved in cold concentrated sulphuric acid to a deep red solution from which water precipitated a dark orange-red powder.

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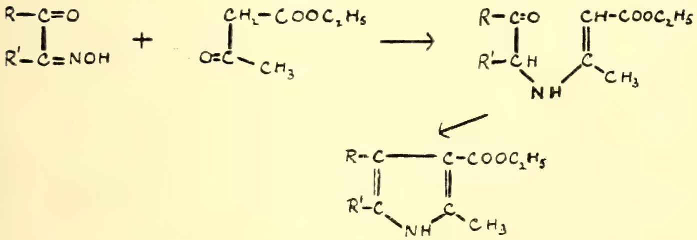
AN EXTENSION OF KNORR'S PYRROLE SYNTHESIS.

By Gregory Bondietti, M.Sc.,

and Francis Lions, B.Sc., Ph.D.

(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

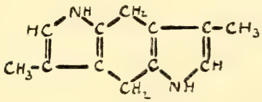
To the group of pyrrole syntheses in which the pyrrole ring is closed in the $\beta\ \gamma$ position, belongs the theoretically important method of Piloty and Robinson, from the azines of enolisable ketones (Piloty, *Ber.* (1910), **43**, 497; Robinson and Robinson, *Journ. Chem. Soc.* (1918), **113**, 639); but the most important is the very general synthesis due to Knorr (*Ber.* (1884), **17**, 1638; *Annalen* (1886), **236**, 317). Knorr originally reduced isonitroso ketones in the presence of acetoacetic ester with zinc and acetic acid, the isonitroso compound being reduced first to an α-amino ketone, which at once condensed with the keto-ester to give an aminocrotonic ester. This then lost water with formation of a pyrrole.



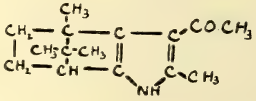
Further careful investigation of the reaction by Knorr and Lange (*Ber.* (1902), **35**, 2998-3008) showed that

better yields of pyrrole could be obtained when the amino ketone was separately prepared and then condensed with a β-keto-ester or β-diketone.

Knorr's synthesis has been widely applied, notably in the synthesis of various hæmopyrroles. However, its extension to the preparation of ring compounds of the hydrogenated indole or carbazole types has been confined almost entirely to one or two examples. Piloty showed that succinyl succinic ester could be condensed with aminoacetone to dimethyldihydropyrrindole (I) (*Ber.* (1910), **43**, 489); whilst Duden has shown that α-aminocamphor can be condensed with acetylacetone to the indole derivative (II) (*Annalen* (1900), **313**, 25; *Ber.* (1901), **34**, 3054).



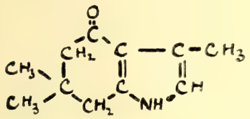
I



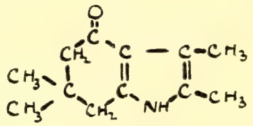
II

In the present work some exploration of the possibility of extending the Knorr synthesis generally to the preparation of compounds of the hydrogenated indole, carbazole and related types has been made by certain preliminary experiments. In the first of these the open chain β-keto ester or β-diketone of Knorr has been replaced by a cyclic β-diketone—dimethyldihydro-resorcinol. After repeated trials it has been found possible to isolate small yields of pyrroles from the reaction mixtures obtained by reducing isonitrosoketones with zinc dust in acetic acid solution in presence of dimethyl dihydroresorcinol. Thus, reduction of isonitrosoacetone in presence of dimethyl-dihydroresorcinol led to formation in 10% yield of 3 : 6 : 6-trimethyl-4-keto-

4:5:6:7-tetrahydro indole (III); whilst by reduction of diacetyl monoxime in presence of dimethyl-dihydro-resorcinol a small yield of 2:3:6:6-tetramethyl-4-keto-4:5:6:7-tetrahydro indole (IV) was obtained.



III



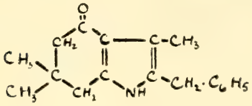
IV

In the same way reduction of α-isonitroso-α-benzyl acetone with zinc dust in acetic acid solution in presence of dimethyldihydroresorcinol led to the formation of 3:6:6-trimethyl-2-benzyl-4-keto-4:5:6:7-tetrahydro indole (V), the yield in this instance being 22%. It was previously found by one or two experiments—described in the experimental section—that α-isonitroso-α-benzyl acetone is specially suitable for the formation of pyrroles in the Knorr synthesis.

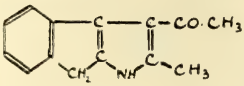
Attempts to prepare pyrroles by reducing α-isonitroso ketones with zinc dust and acetic acid in presence of 1:3-diketohydrindene proved abortive. Condensation appeared to occur readily enough but no definite pure substances could be isolated from the reaction mixtures.

In a second set of experiments the open chain α-isonitroso ketone of Knorr was replaced by a cyclic α-isonitroso ketone—2-isonitroso-1-hydrindone. It was found possible by reducing 2-isonitroso-1-hydrindone with zinc dust in acetic acid solution in presence of acetyl acetone to isolate a small yield of 2-methyl-3-acetyl-4:5-indeno (1:2)-pyrrole (VI); but the corresponding condensation of 2-isonitroso-1-hydrindone with acetoacetic ester could not be satisfactorily achieved.

Finally, an experiment was carried out in which 2-isonitroso-1-hydrindone was reduced with zinc dust in acetic acid solution in presence of dimethyldihydroresorcinol. Although a small yield (about 1%) of a crystalline substance was isolated it was not possible to purify and characterise it.



V.



VI.

The fact that condensation of preformed α-aminoketones with β-keto esters and β-diketones always gives better yields of pyrroles than the method in which an α-isonitroso ketone is reduced in presence of the β-keto ester or β-diketone, suggests that improved yields of pyrroles may be obtained in the above condensations, and it is proposed to carry out further experiments using the former method.

Experimental.

2:4-Dimethyl-3-acetyl-5-benzyl pyrrole.

To a solution of α-isonitroso-α-benzyl acetone (10 g.; *cf.* Sonn, *Ber.* (1907), **40**, 4666) and acetyl acetone (7 g.) in acetic acid (120 g.) was gradually added zinc dust (30 g.) with good cooling, after which the mixture was allowed to stand for thirty minutes and later was heated to 100° for thirty minutes. It was then filtered whilst hot and the filtrate collected in cold water. A white flocculent precipitate separated which was collected and recrystallised from methyl alcohol. There were thus obtained transparent prisms having a very pink tinge, melting at 165-166°, and

readily soluble in methyl alcohol, ethyl alcohol, ethyl acetate, acetic acid and acetone.

Found C = 79·5, H = 7·5%; calculated for $C_{15}H_{17}ON$, C = 79·3, H = 7·6%.

A dilute alcoholic solution of this pyrrole when treated with p-dimethylaminobenzaldehyde and hydrochloric acid at once developes a beautiful red colour (Ehrlich's reaction).

Ethyl-2:4-dimethyl-5-benzyl-pyrrole-3-carboxylate.

Zinc dust (60 g.) was gradually added with constant stirring to a solution of α-isonitroso-α-benzyl acetone (20 g.) and ethyl acetoacetate (15 g.) in glacial acetic acid (220 g.), the temperature not being allowed to rise above 10°. Thirty minutes after completion of the addition the mixture was heated to 90-100° for a further thirty minutes, after which it was filtered and the filtrate poured into cold water. The white solid which separated (12 g.) was collected and recrystallised from methyl alcohol. It was thus readily obtained in large crystals with quite a pronounced pink tinge, melting at 119°.

Found C = 74·6, H = 7·3%; calculated for $C_{16}H_{19}O_2N$, C = 74·7, H = 7·4%.

This pyrrole ester is readily soluble in the usual organic solvents but insoluble in water. In Ehrlich's pyrrole test it gives an immediate definite rose-red coloration.

3:6:6-Trimethyl-2-benzyl-4-keto-4:5:6:7-tetrahydro indole (V).

Zinc dust (30 g.) was gradually stirred into a solution of α-isonitroso-α-benzyl acetone (12 g.) and dimethyl dihydroresorcinol (11 g.) in glacial acetic acid (120 g.), the temperature being kept below 20°. The solution gradually assumed a green colour during the addition of the zinc (one hour). The mixture was then heated at 90-100° for two hours and was then allowed to stand for 48 hours, after which it was filtered and the filtrate

carefully stirred into cold water. The resulting liquid was allowed to stand at 0° for 24 hours, when a yellow flocculent precipitate (5 g.; 22% of theory) had separated. Recrystallised from ethyl acetate it was obtained in faintly yellow micaceous flakes melting at 197°.

Found C = 80·4, H = 8·0%; calculated for $C_{18}H_{21}ON$, C = 80·9, H = 7·9%.

The substance was readily soluble in the usual organic solvents but may be recrystallised from alcohol or ethyl acetate. It does not give Ehrlich's reaction for pyrroles, and does not give any colour with ferric chloride in alcoholic solution.

3:6:6-Trimethyl-4-keto-4:5:6:7-tetrahydroindole (III).

Zinc dust (30 g.) was gradually stirred into a solution of isonitrosoacetone (8 g.) and dimethyldihydroresorcinol (13 g.) in glacial acetic acid (120 g.), the temperature being maintained below 5° throughout the addition. After standing thirty minutes the mixture was finally warmed for thirty minutes and then filtered. Dilution of the filtrate with cold water led to gradual separation of a small amount of the expected pyrrole derivative (2 g.). It was recrystallised with difficulty from ethyl alcohol and thus obtained in small brownish coloured needles, melting at 156°.

Found C = 74·1, H = 8·6%; calculated for $C_{11}H_{15}ON$, C = 74·6, H = 8·5%.

Very soluble in all the usual organic solvents, this substance gives a very definite rose-red coloration in alcoholic solution when treated with Ehrlich's reagent.

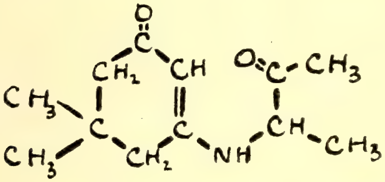
2:3:6:6-Tetramethyl-4-keto-4:5:6:7-tetrahydroindole (IV).

Zinc dust (30 g.) was gradually stirred into a solution of α-isonitroso-α-methyl acetone (10 g.) and dimethyldihydroresorcinol (12·8 g.) in glacial acetic acid (100 g.), the temperature being kept below 10°. Finally, after

standing 30 minutes, and heating at 90-100°, for a further hour the liquid was filtered and the filtrate poured into cold water. Yellow crystals commenced to separate, and after standing overnight at 0° these were collected and recrystallised from ethyl acetate, long yellow needles melting at 228° being thus obtained.

Found C = 75·4, H = 8·9%; calculated for $C_{12}H_{17}ON$, C = 75·9, H = 9·0%.

From the ethyl acetate mother liquors it was possible to isolate in small quantity a product crystallising in colourless prisms and melting at 173-178°. Owing to the small amount present it was not possible rigidly to purify it. An analysis showed C = 66·0%, H = 8·4%. It seems most probable that this substance is similar to the intermediate described by Knorr (*Ber.* (1902), **35**, 2998-3008) and should have the structure (VII).



VII

In such a substance ($C_{12}H_{19}O_2N$) there would be C = 68·9%, and H = 9·0%.

The 2:3:6:6-tetramethyl-4-keto-4:5:6:7-tetrahydroindole above described is readily soluble in the usual organic solvents, and does not give a red coloration when treated with Ehrlich's reagent in alcoholic solution.

2-Methyl-3-acetyl-4:5-indeno (1:2)-pyrrole (VI).

Zinc dust (20 g.) was gradually stirred into a solution of isonitroso-*a*-hydrindone (10 g.) and acetyl acetone (9 g.) in acetic acid (80 g.), the temperature being

prevented from rising by cooling the mixture in ice-water. Immediately after the first addition of zinc dust the solution became bright red in colour—an effect due to the action of zinc and acetic acid on isonitroso-α-hydrindone as it occurred even in absence of acetyl acetone. When excess of zinc had been added the colour gradually disappeared. After warming for 10 minutes on the water bath the mixture was filtered and the filtrate diluted with water. A brown sticky solid separated. Ether was added and the mixture well shaken. After allowing the liquids to separate it was observed that a solid mass had collected at the junction of the two liquids. It was filtered off and recrystallised from much alcohol and thus obtained in very small faintly pink needles melting at 254°.

Found C = 79·1, H = 6·4%; calculated for $C_{14}H_{13}ON$, C = 79·6, H = 6·2%.

This pyrrole derivative is but sparingly soluble in the usual organic solvents but can be recrystallised from much alcohol. It does not give Ehrlich's test for pyrroles.

Additional experiments in which isonitroso acetone, diacetyl monoxime and α-isonitroso-α-benzyl acetone were reduced with zinc dust in acetic acid solution in presence of 1:3-diketohydrindene led only to formation of pasty masses from which no crystalline material could be isolated.

In other experiments isonitroso-α-hydrindone (10 g.) was reduced by addition of zinc dust (25 g.) to its solution in acetic acid (80 cc.) in presence of ethyl acetoacetate (9 g.). It was found possible by the procedure described previously to isolate small amounts of a brownish-red crystalline substance which melted at

195-197°, but was difficult to purify. An analysis showed C = 84·1, H = 6·4%, but these figures are out of agreement for the expected pyrrole.

Finally, in an experiment in which 2-isonitroso-1-hydrindone (6 g.), and dimethyldihydroresorcinol (6) were dissolved in acetic acid (110 cc.) and zinc dust (25 g.) carefully added with cooling, the mixture being finally filtered into water, it was possible to isolate about 1% of a high melting brownish crystalline substance which could be recrystallised from ethyl acetate. The amount was, however, too small to continue further.

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A NOTE ON DIFFRACTION GRATINGS USED WITH GRAZING INCIDENCE.

By O. U. VONWILLER, B.Sc., F.Inst.P.
Professor of Physics, University of Sydney.

(With Plate X.)

(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

Some time ago Mr. W. F. Gale drew my attention to the fact that with a plane reflexion or transmission diffraction grating it is possible to see the Fraunhofer lines in the spectrum of the sun without artificial aid, such as slit, lenses, *etc.* A little experimenting showed that a necessary condition is that the light fall on the grating almost at grazing incidence, while the sharpness of the lines is greater the nearer the diffracted rays are to the normal to the plane of the grating. An examination of the ordinary formula for the plane grating shows at once how this comes about; if θ be the angle between an incident beam and the plane of the grating, and ϕ the angle between the normal to the grating and the diffracted beam giving a maximum for any spectral line, ϕ being taken as positive if diffracted and incident beams are on opposite sides of the normal, we find that if the grazing angle be increased by an amount $d\theta$, small compared with θ, which itself is assumed to be small, the direction of the diffracted beam is changed by $d\phi$ where

$$Cos\ \phi\ d\phi = -\theta d\theta$$

or if $d\theta$ be not small compared with θ

$$Cos\ \phi\ d\phi = -\frac{d\theta}{2}\ (2\theta + d\theta)$$

If a distant source subtend an angle $d\theta$ at the grating, the divergence $d\phi$ of the diffracted rays for a given maximum is given by the above expressions, provided, of course, that θ is small. Unless $Cos\ \phi$ is small, $d\phi$ is obviously less than $d\theta$, the ratio of $d\phi$ to $d\theta$ decreasing as θ and ϕ decrease.

The matter may be discussed even more simply: the ratio of widths of incident to diffracted beams is $\frac{Sin\ \theta}{Cos\ \phi}$, or, if θ be small, $\frac{\theta}{Cos\ \phi}$, so that a lateral contraction, represented by this factor, is produced by the arrangement.

In a paper submitted to the British Astronomical Association, Mr. Gale has given a description of observations made with the solar spectrum, together with the deduction and examination of the above expressions. In this note I present an account of some observations with emission spectra from a sodium flame which illustrate the effect very well.*

In these experiments the grating, a plane metal grating with 14,431 lines to the inch, the length of the ruled surface being 2·7 cms., was placed on a spectrometer table. The focal length of the collimator was 23 cms., and that of the observing camera 53 cms. The plane of the grating was inclined at a small angle to the axis of the collimator and photographs taken of spectra of various orders. The plates used were Ilford Special Rapid Panchromatic. It was found, as the theory indicated, that when wide slits were employed it

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* Since preparing it I have seen a short paper on the use of wide slits at grazing incidence by Morris-Airey, *Phil. Mag.*, 11, 414, 1906, the only reference to the effect which I have found.

was possible to secure fine spectral lines provided that θ and ϕ were small.

Some typical results are recorded on the accompanying plate in which there is an enlargement of 1·55. The width of the slit was about 1·1 mm., θ was 1° 52′, and $d\theta$, the angle subtended by the slit at the centre of the collimator was 16′ 20″.

In Pl. X, fig. 1, are shown, *d*, the direct image of the slit, and *O*, the reflected beam; these were taken simultaneously, enough light passing in front and behind the grating to give the image *d*, so that the ratio of the width of either image to the distance between their centres is $\frac{d\theta}{2\theta}$. As the enlargement of the original plate is 1·55 and the ratio of the focal length of camera to that of collimator is 2·3 the actual slit dimensions are magnified about 3·6 times.

The first, second and third order spectra obtained with this arrangement are shown in the same figure and are indicated respectively by the numbers 1, 2 and 3. Of course the camera had to be set in a different position for each of these, but the magnification was exactly the same as in the direct photograph of the slit.

The angles of diffraction, ϕ, for the stronger line were + 41° 39′, + 19° 14′ 50″ and – 0° 18′ 15″ respectively, and the values of $\theta/\cos\phi$ were 0·047, 0·0346 and 0·0326, the corresponding increase in sharpness as we go from the first to the third order being clearly seen. The source of light was comparatively feeble and the respective times of exposure were 5, 10 and 20 minutes.

The effectiveness of the arrangement is seen in Pl. X, figs. 2 and 3, showing spectra of the first and third order when an intense source was used. The

reversal of each line is clearly seen in the third order with the aid of a magnifying glass, although there has been a considerable loss of sharpness in the reproduction from the original plate. For each of these the time of exposure was one minute, and photographs have been taken of the fourth order, for which $\phi = - 19° 53' 50''$, these, however, requiring much longer exposures.

We see, as the theory indicates, that quite wide slits may be employed without loss of resolving power, and it is not difficult to see that in certain instances there is a distinct advantage in this arrangement over those usually employed, the greater width of slit more than compensating the small width of incident beam. Incidentally, with this setting of the grating the fifth order could be seen quite clearly with the intense beam, a result impossible for large values of θ with this grating space.

The intensity obtained with a given setting naturally depends on the form of the rulings; for example, when this grating was reversed the intensity was greatly reduced in the higher orders.

Even more striking differences between the width of slit and those of the lines in the diffraction spectra were observed with smaller values of θ. Very sharp and bright diffraction spectra were seen when θ was only 35′, but for smaller angles there was a great falling off in intensity; sharp but very faint lines could be seen in the third order when θ was as small as 20′.

An interesting fact is that the sharpness depends hardly at all on the focussing of the collimator, although the camera must always be focussed correctly for parallel rays. As an extreme illustration, Pl. X, fig. 4, shows the first, second and third order spectra obtained when the collimator lens was removed, so that from

each point on the slit a divergent beam fell on the grating; nevertheless the camera focus was the same as with parallel beams falling on the grating. The exposures were 20 min., 60 min. and 120 min. respectively, the light being very faint. Actually the sharpness is greater here than when the collimator lens is used, this being due in part to the fact that the distance between slit and centre of grating was 36 cm. instead of the 23 cm. between slit and centre of collimator lens, thus reducing the value of $d\theta$ by the factor 23/36. Against this we have the divergence of the beam from any part of the slit, but from the data it is readily seen that this produces a comparatively small effect. However, for a given setting, the sharpness, as well as the intensity, when no collimator is used, depends on the dimensions of the grating, striking variations in the apparent complexity of the lines being obtained by altering the width of the ruled surface employed and the mode of illumination of the collimator slit. A treatment of this case will form the subject of a further note.

It may be mentioned here that a sodium flame placed at a distance of 2 or 3 metres, the collimator being entirely removed, gave a sharp pair of lines, with or without the telescope, this being the equivalent to the observations made by Mr. Gale.

A fact which sometimes may be of value is that with the aid of a grating used in this manner the correct adjustment of collimator and telescope in a spectrometer can be readily made by the following method. With the grating set almost at the grazing position, using a wide slit and a source giving a line spectrum, view a spectrum satisfying the condition that ϕ is small. Focus the telescope for this; the telescope is thus

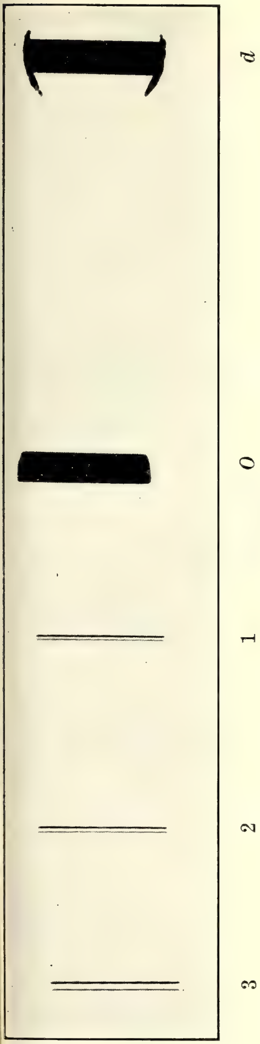

Fig. 1.

Fig. 3.

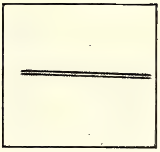

Fig. 2.

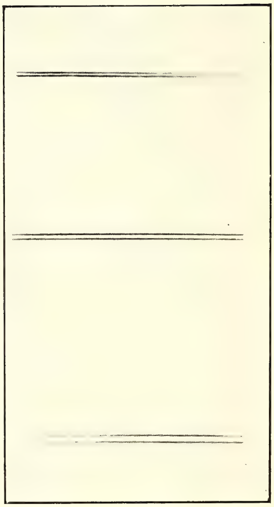

Fig. 4.

PLATE IX.

Fig. 1.—*d*, image of slit by direct light; *O*, image of slit by reflected light; 1, 2, 3, diffraction spectra of first, second and third orders using a faint source.

Fig. 2.—First order spectrum, very bright source.

Fig. 3.—Third order spectrum, very bright source. The line of shorter wave-length is on the left in this case.

Fig. 4.—First, second and third order spectra taken without collimator lens using faint source.

focussed for parallel rays, however badly the collimator may be out of focus. Then turn the telescope to view the slit directly and adjust the collimator until the image is sharply focussed.

It is readily seen that with any grating if a spectrum of some order is obtained at an angle ϕ the sharpness of the lines and the dispersion are independent of the grating space, but of course the sharpness depends on the *total* number of lines.

THE LONGITUDINAL VARIATION OF TIMBER DURING SEASONING.

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(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

Whilst it is a well-known fact that as a general rule the longitudinal shrinkage of timber during seasoning is negligible, nevertheless it is sometimes important that the approximate amount of such shrinkage should be known. According to Koehler[1] it usually varies from 0·1 to slightly over 0·33%, in passing from a green to an oven-dry condition, but mention is made of the fact that Tupelo occasionally shrinks as much as 1·25% and Yellow Pine compression wood up to 3·25%. The radial shrinkage is approximately 50 times as great as the longitudinal shrinkage, and the tangential shrinkage 100 times as great. When the wood is cross grained the apparent longitudinal shrinkage may be considerably higher than normal, due to a component of the lateral shrinkage being introduced. The variation in lateral and longitudinal shrinkage is usually explained theoretically by the assumption that the cell wall is composed of spirally oriented minute longitudinal fibrils,

[1] Koehler, A.: "The Properties and Uses of Wood," McGraw Hill, 1924, p. 51.

between which water is held; loss of moisture from the wood results in the closer packing of the fibrils and hence lateral shrinkage occurs, whilst due to a longitudinal component caused by the inclination of the spiral to the axis, a small amount of shrinkage may occur lengthwise. The shrinkage effects due to alteration in thickness of the water films surrounding the ultramicroscopic particles or micellæ, of which the fibrils are supposed to be formed, is discussed by Forsaith[2]. Brown[3] has suggested that the presence of a longitudinal, sparingly branched, non-hygroscopic, siliceous skeleton in the cell wall would inhibit longitudinal shrinkage or swelling due to moisture variation.

In the present experiment a number of short boards with straight grain were selected, each 10″ long, 4″ wide, and 1″ thick. The ends were coated with paraffin wax, a small amount being scraped off to allow the measuring instruments to rest on the wood. Whilst some 44 of the earlier wood samples were measured with a 12″ vernier caliper, the majority were measured with a specially constructed piece of apparatus, so arranged that measurements were always taken at the same distance from the bottom and one edge of the board. Due to normal lateral shrinkage, there was a slight alteration in the position of the line along which measurements were made, but since the ends of the boards were accurately squared prior to the readings being taken, any error due to this alteration can be neglected. Measurements with this apparatus were made by means of a dial gauge to the nearest 0·0005″.

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[2] Forsaith, C. C.: "The Technology of New York State Timbers," Tech. Publ. No. 18, New York State College of Forestry, 1926.
[3] Brown, F. B. H.: *Bull. Torrey Bot. Club*, 47, 407, 1920.

Measurements were made at regular intervals during the air seasoning of the wood from a green to an air-dry condition for periods varying from six months to three years, and the difference between the original measurement and the mean air-dry figure is regarded as the size variation due to seasoning. This is expressed as a percentage of the total length of the board, the number of specimens of each species, the maximum, minimum, and mean variation in the size being shown in the accompanying table.

The maximum possible error due to the difference between coefficients of linear expansion of the wood and the master gauge used to check the measuring apparatus does not exceed 0·005% over the range of temperature observed.

	No.	Shrinkage %		
		Max.	Min.	Mean.
Acacia melanoxylon, Blackwood	4	0·09	0·01	0·05
Ackama Muelleri, Corkwood ..	2	0·04	−0·03	0·01
Angophora Bakeri, Apple ..	2	0·16	0·09	0·13
Baloghia lucida, Brush Bloodwood	2	0·02	−0·02	0·00
Cardwellia sublimis, Silky Oak ..	2	0·04	−0·02	0·01
Cedrela Toona, Cedar	1	—	—	0·03
Ceratopetalum apetalum, Coachwood	6	0·05	−0·03	0·03
Cryptocarya erythroxylon, Pigeonberry Ash	1	—	—	0·11
C. glaucescens, Brown Beech ..	4	0·13	−0·05	0·04
Daphandra micrantha, Northern Sassafras	2	0·17	0·04	0·10
Diploglottis Cunninghamii, Tamarind	2	0·03	0·02	0·03
Doryphora sassafras, Sassafras ..	9	0·14	−0·01	0·07
Dysoxylum Fraseranum, Rosewood	7	0·09	−0·07	0·02
Endiandra Sieberi, White Corkwood	2	0·05	0·03	0·04
Eucalyptus amplifolia	2	0·17	0·04	0·10

	No.	Shrinkage %		
		Max.	Min.	Mean.
E. Andrewsi, New England Peppermint	4	0·06	0·04	0·05
E. Blakeleyi, Red Gum	2	—	—	0·01
E. botryoides, Bangalay	2	—	—	0·05
E. carnea	2	−0·03	−0·04	−0·03
E. crebra, Narrow-leaved Ironbark	2	−0·05	−0·13	−0·09
E. Dalrympleana, Mountain Gum	2	0·02	−0·03	−0·01
E. Delegatensis, Alpine Ash ..	2	0·19	−0·02	0·08
E. eugenioides, White Stringybark	2	−0·03	−0·05	−0·04
E. fastigata, Brown Barrel ..	2	0·05	−0·04	0·01
E. globulus (*bicostata*), Eurabbie ..	2	−0·01	−0·03	−0·02
E. macrorrhyncha, Red Stringybark	4	0·05	0·01	0·03
E. maculata, Spotted Gum ..	9	0·10	−0·10	−0·03
E. microcorys, Tallowwood ..	13	0·06	−0·10	−0·01
E. obliqua, Messmate	2	—	—	−0·06
E. oreades, Mountain Ash ..	2	0·02	−0·02	0·00
E. paniculata, Grey Ironbark ..	2	−0·01	−0·02	−0·02
E. phellandra, Narrow-leaved Messmate	2	−0·05	−0·04	−0·04
E. pilularis, Blackbutt	11	0·09	−0·08	0·00
E. piperita, Peppermint	3	0·16	−0·06	0·02
E. polyanthemos, Red Box ..	2	0·01	−0·01	0·00
E. punctata, Grey Gum	4	0·09	−0·10	0·01
E. rariflora, Black Box	4	−0·04	−0·01	−0·07
E. resinifera, Red Mahogany ..	11	0·12	−0·10	−0·01
E. rostrata, Murray Red Gum ..	9	0·25	0·04	0·12
E. saligna, Blue Gum	10	0·08	−0·08	−0·01
E. sideroxylon, Red Ironbark ..	2	0·08	0·03	0·05
E. tereticornis, Forest Red Gum ..	2	−0·05	−0·08	−0·07
E. viminalis, Ribbon Gum ..	2	−0·04	−0·07	−0·06
Flindersia Brayleyana, Queensland Maple	4	0·08	−0·06	0·01
Flindersia australis, Colonial Teak	1	—	—	−0·03
Geissois Benthami, Red Carabeen	2	0·03	0·01	0·02
Gmelina Leichhardtii, Beech ..	3	0·10	0·00	0·03
Litsea reticulata, Bolly Gum ..	1	—	—	0·01
Orites excelsa, Prickly Ash ..	2	−0·03	−0·08	−0·05
Schizomeria ovata, Crab Apple ..	2	0·12	0·10	0·11
Sloanea Woollsii, Yellow Carabeen	4	0·05	−0·04	0·01
Stenocarpus salignus, Beefwood	2	0·04	−0·03	0·01
Sterculia acerifolia, Kurrajong ..	2	−0·05	−0·06	−0·05
Syncarpia laurifolia, Turpentine	5	0·08	−0·05	0·01
Tarrietia actinophylla, Stavewood	4	−0·05	−0·12	−0·07
T. argyrodendron, Crow's-foot Elm	2	0·08	−0·01	0·05
Tristania conferta, Brush Box ..	6	0·20	−0·06	0·05
Villaresia Moorei, N.S.W. Maple	2	−0·02	−0·03	−0·02

CONIFEROUS WOODS.

	No.	Shrinkage %		
		Max.	Min.	Mean.
Agathis Palmerstoni, Queensland Kauri	1	—	—	0·26
A. macrophylla, Vanikoro Kauri	2	0·11	0·00	0·06
Araucaria Cunninghamii, Hoop Pine	3	0·14	0·00	0·05
Callitris glauca, Cypress Pine ..	10	0·02	−0·10	−0·05

An examination of the figures shows that in all cases shrinkage did not occur, the figures prefixed with a minus sign indicating that actually swelling apparently occurred. Some woods showed only shrinkage, others only swelling, others again both swelling and shrinkage in the same species. Comparing the Eucalypts with the non-Eucalypts, it is found that the means for 15 Eucalypts indicated swelling and only 11 showed shrinkage, out of a total of 29 species, whereas for 33 non-Eucalypt species, 26 showed shrinkage and swelling occurred in only 6. Of the 62 species, 22 showed shrinkage only, 14 swelling only, and 26 both swelling and shrinkage.

Whereas some of the heaviest woods, *e.g.*, *E. crebra* (67 lbs. per cubic ft.), *E. rariflora* (74 lbs.), *E. paniculata* (66 lbs.), showed swelling only, this also occurred in *Sterculia acerifolia* (30 lbs.) and *Orites excelsa* (41 lbs.). Again shrinkage only was found in *E. sideroxylon* (65 lbs.) and also in *Daphnandra micrantha* (40 lbs.). Kauri is usually credited with having the maximum longitudinal shrinkage, and although one sample of

Queensland Kauri showed 0·26%, one specimen of Vanikoro Kauri showed no movement. The range of shrinkage of all specimens was zero to 0·26% (*Agathis Palmerstoni*), and of swelling zero to 0·13% in (*E. crebra*). It should be clearly recognised, however, that the comparatively few specimens of each species examined, in some cases only one, does not allow of any generalisation to be made, since obviously the range of variation will no doubt be extended with further records.

The swelling effect was observed in specimens which were measured with the vernier calipers as well as in those measured with the dial gauge apparatus.

The only explanation which can be suggested is that internal stresses developed during seasoning may cause an elongation of the wood under certain conditions, and this aspect is being further investigated.

In conclusion, I wish to acknowledge the valuable assistance rendered by Mr. F. B. Shambler, of the Museum staff, during the progress of this work.

EXPERIMENTS ON THE DAILY SHRINKAGE AND SWELLING OF WOOD.

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(With One Text-figure.)

(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

In connection with an investigation of the shrinkage and swelling of timber when exposed to atmospheric conditions, an experiment was made to determine the maximum amount of size variation liable to occur in certain timbers in the Sydney district. Since size and moisture content are definitely correlated, the experiment also indicated the maximum and minimum moisture content.

Six timbers were selected, one quarter-cut (*i.e.*, parallel to the rays) and one backed-off (*i.e.*, at right angles to the rays) piece being used of each species. Three of these species comprised coniferous softwoods, namely, Cypress "Pine" (*Callitris glauca*), Queensland Kauri (*Agathis Palmerstoni*), and Baltic "Pine" (*Picea excelsa*). Three were hardwoods, Tallowwood (*Eucalyptus microcorys*), Blackbutt (*E. pilularis*), and Alpine Ash (*E. Delegatensis*).

In order to obtain the maximum variation in size in the shortest time the specimens were cut 1″ in length

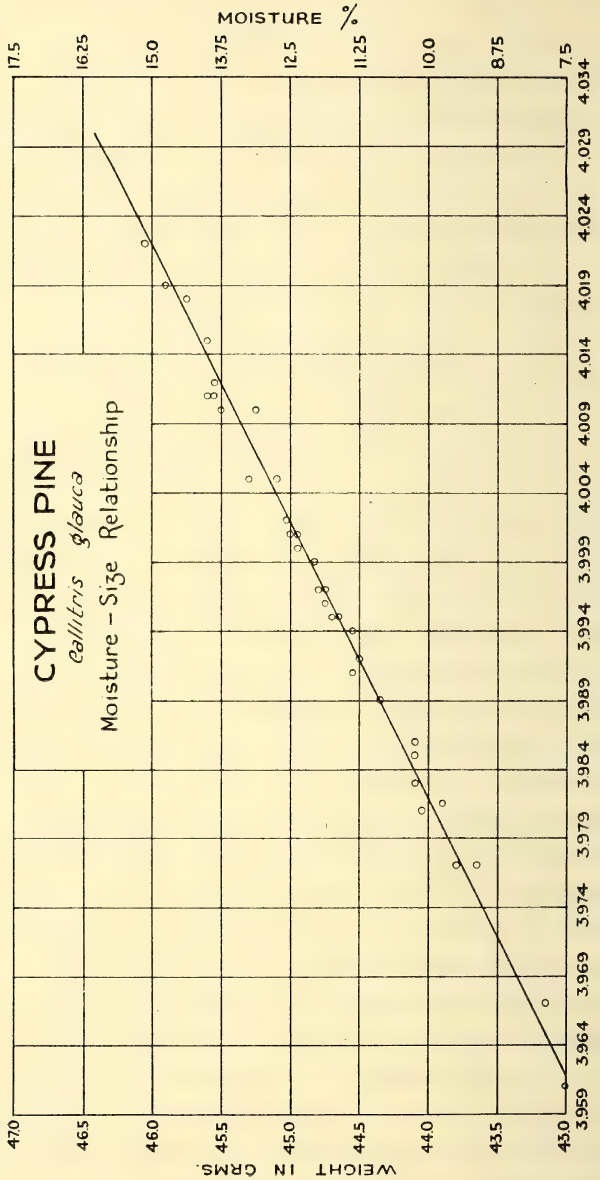
in the direction of the grain, 4″ wide and 1″ thick, and the end grain was left uncoated.

Measurements were made with a shrinkage micrometer to the nearest 0·001″, at 9 a.m., 1 p.m., and 5 p.m. daily, with the exception of week-ends and holidays, over a period from 31/7/1930 to 11/9/1931; in all, over 7,000 readings being taken. At frequent intervals the specimens were also weighed, and by determining the oven-dry weight at the end of the experiment, it was possible to determine the moisture content present at each weighing. By plotting the moisture content thus calculated and the size of the specimen it was possible to determine the relationship between these factors, and hence to determine the moisture content corresponding to any dimension of the specimen. An example of the size and moisture content relationship for quarter-cut Cypress Pine is shown in Figure I.

The specimens were placed alternately in eight positions for periods of about three weeks, each situation giving different conditions. Wet and dry bulb temperatures were recorded at each station and the relative humidity determined.

Table 1 shows the maximum and minimum moisture percentages found at each of the eight stations. An examination of the results shows that Tallowwood varied least, the moisture content ranging from 9·2 to 15·1%, whereas Baltic varied from 5·6 to 18·4%. Cypress Pine also showed a comparatively small range, namely, 7·5 to 15·1%, similarly Blackbutt 7·6 to 15·8%, Alpine Ash 5·8 to 16·2%, and Queensland Kauri from 4·5 to 18·1%. There does not appear to be any connection between the direction of the cut and the variation in moisture content; the same timber at one station

FIGURE I.


CYPRESS PINE
Callitris glauca
Moisture - Size Relationship
MOISTURE %
17.5
16.25
15.0
13.75
12.5
11.25
10.0
8.75
7.5
WEIGHT IN GRMS.
47.0
46.5
46.0
45.5
45.0
44.5
44.0
43.5
43.0
SIZE IN INCHES
3.959
3.964
3.969
3.974
3.979
3.984
3.989
3.994
3.999
4.004
4.009
4.014
4.019
4.024
4.029
4.034

showed a greater variation when quarter-cut, at another station, the converse occurred. The minimum moisture figures were found at station (4), southerly aspect, evidently as the result of a hot dry wind, and the maximum at stations (1) and (3). As would be expected, the minimum variation occurred at stations (5), (6), (7) and (8).

Table 2 gives the mean moisture percentages at each station, at 9 a.m., 1 p.m., and 5 p.m., together with the mean relative humidities. Whereas there was practically no alteration in the moisture content of the wood during the day in inside positions (stations (5), (6), (7) and (8)), the mean alteration not exceeding 0·1%, there was a mean reduction of 0·8% at station (3) in which the samples were exposed to an afternoon sun. At station (2), with an easterly aspect, the mean reduction amounted to 0·9% between 9 a.m. and 1 p.m., with an increase of 0·2% between 1 p.m. and 5 p.m. In an outside position protected from the sun, there was a decrease of 0·5% between 9 a.m. and 1 p.m., and a further decrease of 0·2% during the afternoon. With a southerly aspect the morning decrease amounted to 0·5% without further reduction from 1 p.m. to 5 p.m.; whilst facing west the morning decrease of 0·3% was less than that in the afternoon, namely, 0·5%.

Dealing with the individual timbers, the minimum moisture variation was found in Tallowwood, the greatest alteration being only 0·3% at station (2). Similarly, Blackbutt showed a variation of 0·5% at station (2), Cypress Pine 0·7% at stations (2) and (3), Alpine Ash 0·9% at station (3), Kauri 1·4% at station (3), and Baltic 1·6% at station (3).

The actual shrinkage in inches can be determined from Column 5, Table 4.

TABLE 1.

Maximum and Minimum Percentages of Moisture found at each of Eight Stations.

	1		2		3		4		5		6		7		8	
	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.
Blackbutt Q	15·8	11·6	13·8	8·5	14·8	9·3	13·7	7·8	14·4	13·5	13·0	11·3	12·4	11·3	13·1	10·9
,, B	15·4	11·0	13·4	7·6	15·0	9·4	13·0	7·9	14·7	13·1	12·9	11·4	12·0	11·2	13·1	10·9
Tallowwood Q	14·9	12·4	13·1	9·3	13·5	10·2	12·8	9·3	13·7	13·1	12·4	11·8	11·9	11·3	13·1	11·5
,, B	15·1	13·1	13·7	9·3	13·4	10·9	13·1	9·2	14·6	13·4	12·5	11·8	12·0	11·2	13·3	11·8
Alpine Ash Q	15·1	9·9	13·5	7·2	16·2	7·7	13·7	5·8	13·6	12·4	12·9	10·5	12·3	11·2	12·5	10·3
,, B	15·1	9·8	13·6	7·0	16·5	7·7	13·9	6·2	13·9	12·7	12·9	10·6	12·2	11·2	12·7	10·4
Cypress Pine Q	14·0	11·0	13·3	7·8	15·1	8·0	13·1	7·5	13·1	12·4	12·9	10·5	12·3	11·1	12·6	10·6
,, B	13·9	10·7	13·2	7·6	14·5	8·3	12·9	7·5	12·9	11·9	12·4	10·6	12·0	11·1	12·4	10·6
Q'land Kauri Q	16·9	11·0	14·5	6·7	17·7	7·6	14·6	6·0	14·5	13·7	13·7	11·2	12·9	11·2	13·5	10·3
,, B	15·4	10·2	14·6	7·2	18·1	7·1	14·7	4·5	13·9	12·9	13·8	11·0	12·9	11·7	13·6	10·5
Baltic Q	15·6	10·4	14·8	7·0	18·0	7·0	14·8	5·7	14·0	12·9	14·1	11·1	13·0	12·0	13·8	10·6
,, B	15·2	10·5	14·6	6·6	18·4	6·6	14·5	5·6	13·7	12·7	13·8	11·1	12·7	11·8	13·9	10·3

Station 1. Outside, under cover, not exposed to sun.
,, 2. Outside, easterly aspect, under cover, exposed to sun until 12 noon.
,, 3. Outside, westerly aspect, under cover, exposed to sun from 1 p.m. till 5 p.m.
,, 4. Outside, southerly aspect, under cover, exposed to sun until 9 a.m.
,, 5. Inside, room with northerly aspect, well ventilated.
,, 6. Inside, basement with easterly aspect.
,, 7. Inside, basement, not well ventilated.
,, 8. Inside, basement, with southerly aspect, well ventilated.

TABLE 2.

Mean Percentage of Moisture in Timbers at Different Periods, namely, 9 a.m., 1 p.m., and 5 p.m. Stations similar to those in Table 1.

	Station 1.			Station 2.			Station 3.			Station 4.		
	9 a.m.	1 p.m.	5 p.m.	9 a.m.	1 p.m.	5 p.m.	9 a.m.	1 p.m.	5 p.m.	9 a.m.	1 p.m.	5 p.m.
Blackbutt Q	14·1	13·8	13·8	11·2	10·7	10·7	12·3	12·2	11·9	11·4	11·0	10·9
,, B	13·3	13·1	13·0	10·8	10·3	10·3	12·1	12·1	11·7	11·2	11·0	10·9
Tallowwood Q	13·6	13·5	13·5	11·3	11·0	11·0	11·8	11·9	11·8	11·2	11·1	11·1
,, B	13·9	14·0	14·0	11·7	11·5	11·4	12·0	12·1	12·0	11·5	11·4	11·3
Alpine Ash Q	12·9	12·4	12·3	10·9	10·1	10·2	12·4	12·0	11·5	10·9	10·5	10·4
,, B	13·0	12·7	12·5	11·6	10·7	10·8	12·3	12·2	11·5	11·0	10·4	10·3
Cypress Pine Q	13·0	12·9	12·7	11·2	10·4	10·5	12·1	11·9	11·4	11·1	10·8	10·7
,, B	12·8	12·5	12·4	10·9	10·1	10·2	11·8	11·6	11·2	11·1	11·0	11·1
Q'land Kauri Q	14·4	13·9	13·6	11·2	10·0	10·2	13·2	12·5	11·8	11·6	10·5	10·7
,, B	13·8	13·0	12·7	11·8	10·4	10·8	13·2	12·4	11·8	11·4	10·6	10·8
Baltic Q	13·6	13·3	12·9	12·0	10·4	11·0	13·5	12·7	12·0	11·6	10·8	10·9
,, B	13·7	13·0	12·9	11·8	10·3	10·8	13·5	12·5	11·9	11·2	10·6	10·9
Mean	13·5	13·2	13·0	11·4	10·5	10·7	12·5	12·2	11·7	11·3	10·8	10·8
Relative Humidity % ..	76	59	79	61	58	63	71	58	65	56	59	62

TABLE 2.—*Continued.*

Mean Percentage of Moisture in Timbers at Different Periods, namely, 9 a.m., 1 p.m., and 5 p.m.—Continued.
Stations similar to those in Table 1.

	Station 5.			Station 6.			Station 7.			Station 8.		
	9 a.m.	1 p.m.	5 p.m.	9 a.m.	1 p.m.	5 p.m.	9 a.m.	1 p.m.	5 p.m.	9 a.m.	1 p.m.	5 p.m.
Blackbutt Q	14·0	14·0	14·0	12·1	12·1	12·1	12·0	12·0	11·9	12·4	12·4	12·4
,, B	13·8	13·7	13·7	12·1	12·1	12·1	11·8	11·8	11·8	12·3	12·3	12·3
Tallowwood Q	13·4	13·6	13·5	12·0	12·0	12·0	11·7	11·7	11·7	12·6	12·6	12·6
,, B	14·2	14·2	14·2	12·3	12·3	12·3	11·6	11·6	11·6	12·8	12·8	12·8
Alpine Ash Q	12·6	12·7	12·6	11·9	11·8	11·8	11·8	11·5	11·4	11·9	11·9	12·0
,, B	13·1	13·1	13·0	12·0	11·9	11·9	11·9	11·9	11·8	12·0	12·0	12·0
Cypress Pine Q	12·8	12·8	12·7	11·7	11·6	11·7	11·9	11·9	11·8	12·1	12·0	12·0
,, B	12·7	12·6	12·6	12·0	11·9	11·9	11·7	11·7	11·6	11·9	11·9	11·9
Q'land Kauri Q	14·0	14·0	13·9	12·6	12·6	12·6	12·5	12·5	12·4	12·7	12·6	12·7
,, B	13·4	13·3	13·3	12·6	12·6	12·8	12·5	12·5	12·4	12·7	12·7	12·7
Baltic Q	13·4	13·4	13·3	13·0	12·9	12·9	12·8	12·8	12·7	12·9	12·9	12·9
,, B	13·3	13·3	13·2	12·7	12·6	12·7	12·5	12·5	12·4	12·8	12·7	12·8
Mean	13·4	13·4	13·3	12·3	12·2	12·2	12·1	12·0	12·0	12·4	12·4	12·4
Relative Humidity % ..	68	—	64	71	71	78	71	68	70	70	70	74

TABLE 3.

Maximum Shrinkage or Swelling and Corresponding Moisture Variations, found between 9 a.m. and 1 p.m. in any one day.

	Shrinkage or Swelling.		Moisture Variation %.	
	Inside.	Outside.	Inside.	Outside.
Blackbutt Q. ..	0·005″	0·013″	0·6	1·4
,, B. ..	0·005″	0·019″	0·5	1·7
Tallowwood Q. ..	0·002″	0·007″	0·3	1·0
,, B. ..	0·002″	0·007″	0·2	0·8
Alpine Ash Q. ..	0·008″	0·022″	0·9	2·6
,, B. ..	0·015″	0·039″	1·1	2·8
Cypress Pine Q. ..	0·006″	0·019″	0·8	2·4
,, B. ..	0·006″	0·020″	0·7	2·3
Q'ld. Kauri Q. ..	0·009″	0·022″	1·5	3·6
,, B. ..	0·008″	0·031″	1·1	4·1
Baltic Q.	0·008″	0·023″	1·4	4·1
,, B.	0·013″	0·043″	1·4	4·5

TABLE 4.

	1	2	3	4	5	6
Blackbutt	Q	14·9	7·6	11·3	0·0023	51·3
,, ...	B	14·7	8·3	11·5	0·0028	56·3
Tallowwood	Q	14·9	9·3	12·2	0·0017	65·3
,, ...	B	15·1	9·5	12·3	0·0022	62·1
Alpine Ash	Q	16·3	5·8	11·1	0·0021	39·8
,, ...	B	16·4	6·2	11·3	0·0035	40·4
Cypress Pine	Q	15·1	7·5	11·2	0·0020	45·4
,, ...	B	14·6	7·5	11·1	0·0022	44·5
Queensland Kauri ..	Q	18·1	6·0	12·1	0·0015	28·7
,, ..	B	18·2	6·0	12·1	0·0019	27·5
Baltic	Q	18·0	5·6	11·8	0·0014	28·6
,, ...	B	18·6	5·6	12·1	0·0024	23·1

1. Q=" Quarter cut." B=" Backed off."
2. Maximum moisture percentage occurring during experiment.
3. Minimum moisture percentage occurring during experiment.
4. Mean moisture percentage occurring during experiment obtained from $\frac{\text{max.}+\text{min.}}{2}$
5. Variation in width in inches, per inch, per 1% moisture alteration.
6. Weight per cubic foot in pounds, air-dry volume and weight.

It is a common belief amongst timber users that flooring should be laid preferably in the afternoon, since the wood which has absorbed moisture overnight has by then shrunk to its minimum size. The maximum lateral shrinkage found between 9 a.m. and 1 p.m. for any one day is shown in Table 3. For example, Tallowwood showed a maximum lateral shrinkage of only 0·002″ for inside positions, and even outside the variation was only 0·007″, for a section of a 4″ board, an amount which is absolutely negligible. Moreover, these figures are extremes since they were obtained from very short sections with almost a maximum amount of end-grain freely exposed, and would be considerably less than those obtained from boards of even moderate length.*

* In order to determine the relative amount of movement in specimens of greater lengths in comparison with these used in this experiment, short boards 4″ in width and 1″ thick of Tallowwood, Alpine Ash and Baltic were selected. Two sections were cut from each, one measuring 10″ long and the other 1″ long. The widths of larger section were measured across the middle and also at 1″ from the end, at frequent intervals. The following average size variations, either shrinkage or swelling, were obtained:

	10″ × 4″ × 1″		1″ × 4″ × 1″
	End.	Middle.	
Tallowwood	0·0016″	0·0017″	0·0056″
Alpine Ash	0·0085″	0·0031″	0·0226″
Baltic	0·0077″	0·0076″	0·0189″

Neither Tallowwood nor Baltic showed much difference between the width variation of the end and middle, although Alpine Ash showed a greater end movement. The mean movement of the centre of the board was approximately two and a half times less than the movement of the 1″ section in the case of Baltic, three times with Tallowwood, and seven times with Alpine Ash.

Cypress Pine gave a maximum shrinkage of 0·020″ and 0·006″ for outside and inside positions respectively, Blackbutt 0·019″ and 0·005″, Kauri 0·031″ and 0·009″, Alpine Ash 0·039″ and 0·015″, Baltic 0·043″ and 0·013″. Between 1 p.m. and 5 p.m. the maximum daily shrinkage was as follows: Tallowwood 0·007″ and 0·002″ for outside and inside positions respectively, Blackbutt 0·019″ and 0·003″, Cypress Pine 0·019″ and 0·003″, Kauri 0·020″ and 0·005″, Alpine Ash 0·029″ and 0·007″, Baltic 0·026″ and 0·008″. Stored in a building therefore the daily morning or afternoon shrinkage, even in the timbers which showed the greatest variation, namely, Alpine Ash and Baltic, scarcely exceeded 0·01″ in 4″. Without doubt, many open joints in flooring boards are caused through storing thoroughly seasoned timber in buildings when the humidity is high, due to moisture evaporated from wet plaster, concrete, *etc.* It does not appear possible therefore for daily variations in moisture, due to normal atmospheric conditions, to be worth considering.

Table 4 shows the maximum, minimum, and mean moisture contents of the wood samples, together with the width variation per inch found to occur in each sample for an alteration of 1·0% in the moisture content. The densities of the woods are also given. It is interesting to note that in some timbers the variation between the movement of the "quarter-cut" and "backed-off" is almost negligible; *e.g.*, Cypress Pine, Tallowwood, Blackbutt, and Queensland Kauri. The greatest variation occurs in Alpine Ash and Baltic. The maximum alteration in size corresponding to a 1·0% moisture gain or loss was 0·0035″ in backed-off Alpine Ash, and the minimum 0·0014″ in quarter-cut Baltic.

Summary.

A series of measurements was made three times daily over a period of about fourteen months to determine the lateral shrinkage and swelling of short "quarter-cut" and "backed-off" sections of six different timbers. The wood samples were placed in eight different positions in order to obtain as variable conditions as possible. The variations in size and moisture content are correlated and tables show the maximum and minimum percentages of moisture found at each station, the mean moisture content at each period at which measurements were made, the maximum swelling and shrinkage and the corresponding alteration in moisture content between 9 a.m. and 1 p.m. in any one day, and the lateral movement corresponding to a change of 1·0% in the moisture content of the wood.

Since short sections were used the size variation was considerably greater than that likely to occur in boards, but even in such short sections the maximum daily movement for timber such as Baltic, stored inside, was not found to exceed 0·013″ in 4″, and 0·043″ for timber stored outside, between 9 a.m. and 1 p.m., whilst in a timber such as Tallowwood the size variation did not exceed 0·002″ and 0·007″ for inside and outside positions respectively, an amount which is practically negligible.

In conclusion, acknowledgment is due to Mr. F. B. Shambler, of the Museum staff, for his very considerable assistance in making the necessary measurements.

APPLICATION OF OPTICAL SPECTROSCOPY TO ANALYSIS OF TUMOUR TISSUE.*

By Winifred R. Mankin, M.Sc.

(Communicated by Professor O. U. Vonwiller.)

(With Plate XI.)

(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

A method has been described of qualitatively determining the presence of metals in a specimen of dried tumour tissue. Besides the metals iron, magnesium, sodium, potassium and calcium which are commonly known to occur in such tissue, there is evidence of the presence of aluminium, chromium, copper, lithium, manganese, strontium and zinc. Judging from the relative intensities of the lines, aluminium, lithium and strontium are present in much greater proportion than the other rare constituents.

No *raies ultimes* of the following elements have been found: antimony, beryllium, boron, cadmium, cæsium, cobalt, indium, iridium, lead, nickel, palladium, platinum, rhodium, silicon, thallium, titanium, zirconium, lutecium.

A report is given summarising the evidence of the *raies ultimes.*

The investigation has been undertaken with the object of determining both qualitatively and quantitatively the heavy elements of animal tissue. The presence of the

* This work was carried out under the control of the Cancer Research Committee of the University of Sydney, and with the aid of the Cancer Research and Treatment Fund.

following elements, barium, bismuth, molybdenum, vanadium and rubidium, has been left indefinite owing to the presence of lines of the more commonly occurring metals of the tissue (for example, iron), or of the metal of the electrode, at the same wave lengths as those of the *raies ultimes* of the above elements.

Methods of Investigation.

Three methods by which this analysis can be done are, the ordinary procedures in analytical chemistry, optical spectroscopy and X-ray spectroscopy.

The method which has been selected for trial is that of optical spectroscopy. It was decided to use electric means of excitation by some modification of an arc or spark circuit: the former which gives a less complex spectrum than the latter was chosen. The principal of the Pfund arc obviously could not be applied, nor could one use electrodes of the tissue. Professor Vonwiller then suggested that metal electrodes be used and that the lower (which it has been found advisable to make the positive one) should have a small cone-shaped depression drilled in it (for description see *Chemical Engineering and Mining Review*[1]). In this cavity a portion of the dried tissue is placed, and as this amount of material takes roughly 15 seconds to ash, the number of renewals will of course depend on the time during which one wishes to expose the photographic plate to the tissue spectrum. In some trials 110 volts D.C. is used, the current employed being about 6 amps., while in others 250 volts D.C. supply is used, the current then being about 3 amps. The higher voltage gives a steadier arc, but when using the E3 Hilger quartz spectroscope (which at a later stage was put at my disposal), it was not available owing to the unsuitable wiring of the building.

Numerous electrodes were used, but silver was found the most suitable. Copper was sometimes used as there are regions in its spectrum which have relatively fewer lines than similar regions in the silver spectrum.

Method of Detection of Metals.

The arc spectrum given by the electrodes is taken, and underneath this the spectrum which is given with the added tissue. One assumes that the lines which are not common to both are due to the tissue. On this is superimposed a spectrum taken under similar conditions to the above, of the element whose presence or absence it is wished to determine; an estimate is made visually of whether its *raies ultimes* are present in the tissue or not. For increased convenience and accuracy, Professor Vonwiller suggested that enlargements of the plates be made. Through the courtesy of Professor Stump, who generously allowed the use of the enlargement apparatus in his department, the plates were enlarged five times and printed in the positive in one operation. This is a very real advantage as no detail of structure is lost and the spectrum from the quartz spectroscope, which ranges from 7,000 A.U. to 4,000 A.U., is now about four feet in length. Other methods of determining wave length are discussed elsewhere.[(1)]

Concerning Quantitative Analysis.

With a technique similar to that already described, some preliminary experiments have been conducted on the relative intensity of certain sodium and potassium lines to those of certain magnesium lines in known mixtures of salts of sodium, potassium, calcium, magnesium and phosphorus; also on the relative intensity of certain gold and silver lines in known

alloys of these two metals. Some interesting results have been obtained which it is hoped to communicate at a later date. It is thought, however, that more satisfactory results can be obtained by comparing the intensity of lines corresponding to similar transitions in elements which give like spectra, than by arbitrarily selecting lines; work is being carried out at present by the usual methods of spectrum analysis on silver gold alloys of known composition.

Some Observations on the Spectra of Tissue.

Consideration of the photographs reveals some interesting points. The common effect of the inconsistency of the variation in intensity of lines is seen. For example, lithium line 6,708 appears stronger in the silver and tissue $3\frac{1}{2}$ minutes' exposure than in the silver and tissue 1 minute exposure. Similarly the calcium lines 5,270-62 are stronger in the former than the latter, while the iron lines between 2,938 and 3,030 have about the same intensity in the two spectra. On comparing a spectrum of copper and tissue with that of silver and tissue taken with the same exposure, one finds that, although the strong calcium lines 3,969 and 3,934 appear to have the same intensity in the two spectra, yet the iron lines 2,938-3,030 are represented in the copper spectrum but faintly, while much more intensely in the silver spectrum.

The accompanying photographs give an idea of the quality of the work done by enlargement of the original plates.

Plate XI, Fig. 1, is a spectrum given by the silver electrodes for 1 minute exposure, and below that is a spectrum of silver plus tissue for the same time of exposure. The lines not common to both are marked

according to the element to which they belong. Wherever a line of a commonly occurring element has also corresponded with a *raie ultime* of a rare element which may be present in tissue it is taken as belonging to the former.

The five magnesium lines on the extreme left of Fig. 1 are 2,783·08, 2,781·53, 2,778·36, 2,779·94 and 2,776·80. The dispersion here is approximately 2 A.U. = 1 millimetre. Further to the right can be seen four lines of phosphorus, 2,550·0, 2,553·37, 2,535·74 and 2,534·12. The dispersion here is approximately 1·4 A.U. = 1 millimetre. An examination of the spectra shows the well known pole effect, also the common effect of alteration in intensity, for the silver lines are on the whole less intense in the silver plus tissue spectrum than the one above it.

Plate XI, Fig. 2, shows a portion of a copper spectrum from 4,063 A.U. to 3,248 A.U. The top one is a copper spectrum and the lower copper and tissue; both were taken with an exposure of five seconds. It will be seen that the copper spectrum is relatively rich in lines bearing out the statement that copper on the whole is less suitable as a carrier than silver. The cyanogen band starting at 3,884 A.U. is an example of how continuous spectrum from an abundant constituent in the tissue prevents the detail of lines in this region being examined.

Evidence on Which Detection of Metals is Based.

Sometimes a *raie ultime* of a metal has been found present in the electrode plus tissue, and also in the electrode. Its presence in the tissue can usually be determined by the greater concentration of the line in the former. However, if this is not the case, then an electrode of another metal free from lines in this region is used.

Four sources of reference have been used for *raies ultimes.* These are Tr. Negresco (*a*), E. Baly (*b*), Critical Tables (*c*) and Hilger (*d*).

Aluminium.—3,962, 3944 (*a, b, c, d*) present (p.) in silver plus tissue, also present in silver. Present in copper plus tissue, not present (n.p.) in copper.

Chromium.—3,594 (*b*), p. in silver and tissue, n.p. in silver, 4,255 (*c, d*) p., 2,836 (*c*) n.p., 5,209, 5,206 (*b, c*) masked by silver line 5,209. 4,290 (*a, b, c*) if present masked by iron. 3,605 (*d*) p., 3,579 (*d, b*) p., 2,850 (*c*), 2,843 (*c*), n.p.

Copper.—3,248 (*a, b, c, d*), 3,274 (*a, b, c, d*) if p., masked by continuous spectrum. 5,218 (*a, b*) if p., masked by continuous spectrum. 5,153 (*a, b*) if p., masked by sodium. 5,106 (*a, b*) p., but also p. in silver. 2,136 (*c*) and 2,192 (*c*) both p.

Lithium.—6,708 (*d, b, c*) p. 4,602 (*b*) n.p. 3,233 (*d, c, b*) n.p. 6,104 (*d*) n.p.

Manganese.—4,031 (*b, c, d*) if p., masked by iron. 4,035 (*d, b*) p. 2,594 (*b, c, d*) n.p. 2,576 (*a, c, d, b*) n.p. 2,606 (*b, c, d*) n.p. 4,824 (*b*) p., but also in silver. 4,783 (*b*) n.p. 4,754 (*b*) p. 2,594 (*c, d, b*) n.p. 2,576 (*c, d, b*) n.p.

Strontium.—4,608 (*b, d*) p. 4,078 (*d, c, b*) p. 4,306 (*b*) if p., masked by calcium. 4,216 (*c, d, b*) if p., masked by calcium.

Zinc.—4,722 (*d, b, c, a*) p., but there is also a *raie ultime* of bismuth at this wave length. It is attributed to zinc which has more evidence in favour of it. 4,811 (*a, b, c, d*) p. 3,345 (*a, b, c, d*) n.p. 4,680 (*d, b, a*) n.p. 3,303 (*d, a*) if p., masked by sodium. 2,558, 2,138 (*a*) n.p., 2,502 (*a*) if p., masked by magnesium.

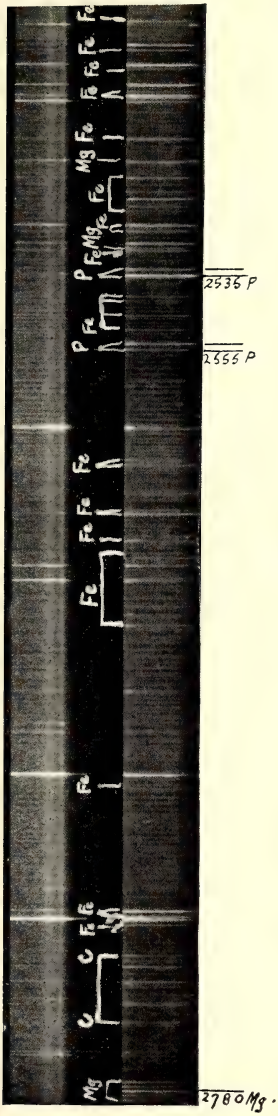

2535 P
2555 P
2780 Mg.

Fig. 1.

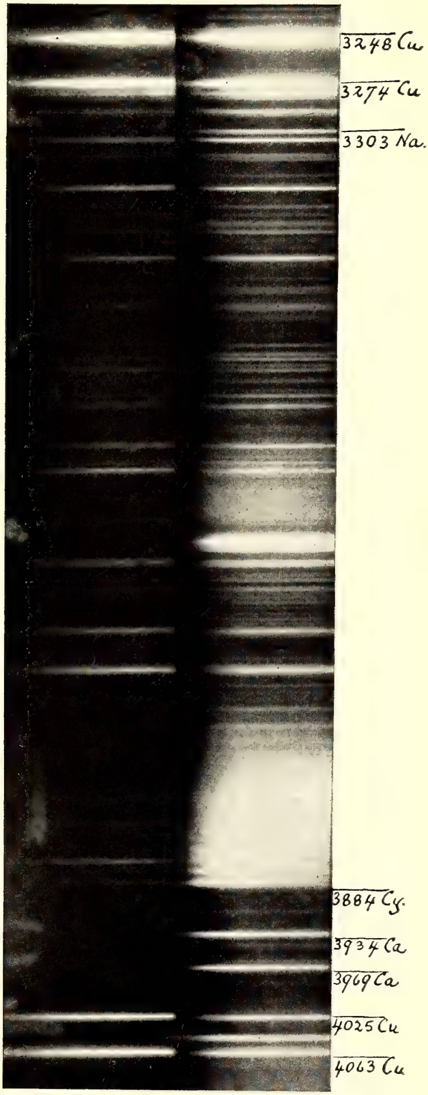

3248 Cu
3274 Cu
3303 Na.
3884 Cy.
3934 Ca
3969 Ca
4025 Cu
4063 Cu

Fig. 2.

In conclusion, I wish to take this opportunity of expressing my thanks for material, and the loan of apparatus, to Professors Davies, Earl, Eastaugh, Fawsitt and Stump, Dr. Chapman and Mr. C. W. Morris. In particular I wish to thank Professor O. U. Vonwiller, under whose direction this work was done, for his encouragement, practical assistance and the apparatus which he put at my disposal, and also for very many suggestions throughout the entire progress of this work.

References.

(1) W. Mankin: "Application of Optical Spectroscopy to Analysis of Tissue", *Chemical Engineering and Mining Review*, Vol. 24, No. 280, 1932, page 142.

(2) Tr. Negresco: Thesis à la Faculté des Sciences de l'Université de Paris, 1927, pages 73-83.

(3) E. Baly: *Spectroscopy*, Vol. II, 1927, page 150.

(4) *Critical Tables*, Vol. 5, 1929, page 322.

Explanation of Plate XI.

Fig. 1.—Above: Spectrum given by silver electrodes (exposure one minute). Below: Spectrum given by silver electrodes and tissue (exposure one minute).

Fig. 2.—Above: Spectrum given by copper 4,063 A.U.–3,248 A.U. (exposure five seconds). Below: Spectrum given by copper 4,063 A.U.–3,248 A.U. and tissue (exposure five seconds).

RESEARCHES ON INDOLES.

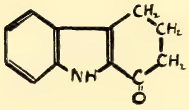
PART III.

APPLICATION OF THE JAPP-KLINGEMANN REACTION TO CYCLIC β-KETO-ACIDS.

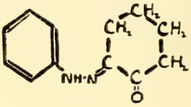
By FRANCIS LIONS, B.Sc., Ph.D.

(Read before the Royal Society of New South Wales, Dec. 7, 1932.)

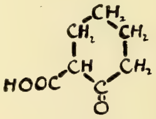
In a recent paper Jackson and Manske (*J.A.C.S.* (1930), **52**, 5029) described the preparation of γ-(2-carbethoxy-3-indolyl)-butyric acid, and observed that heat treatment of this acid led to formation of appreciable quantities of 1:keto-1:2:3:4-tetrahydrocarbazole (I). Coffey (*Rec. Trav. Chim.* (1923), **42**, 528) had previously shown that this substance could be readily obtained by cyclisation with acid of the monophenylhydrazone of cyclohexan-1:2-dione (II), which, in turn, was easily obtainable by the action of benzene diazonium chloride on the sodium derivative of oxymethylene cyclohexanone.



I



II



III

Now it is well known that diazonium salts react with the alkali salts of α-mono-substituted β-ketoacids to form substitued hydrazones, carbon dioxide being simul-

taneously eliminated (*cf.*, for example, Japp and Klingemann, *Annalen,* **247**, 218).

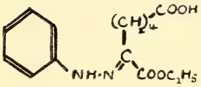
$$R{-}N_2Cl + \overset{CO\cdot R'}{\underset{COONa}{CH}}{-}R'' \longrightarrow R\cdot NH\cdot N{=}\overset{CO\cdot R'}{C}{-}R'' + NaCl + CO_2$$

It is thus at once apparent that a ready method of preparation of the monophenylhydrazone of cyclohexan-1:2-dione should be that in which benzene diazonium chloride is permitted to react with an alkali salt of cyclohexanone-2-carboxylic acid (III). Confirmation of this point of view is to be found in the fact that cyclopentan-1:2-dione monophenylhydrazone (V) has already been prepared by adding a solution of benzene diazonium chloride to a solution of cyclopentanone-2-carboxylic acid and then adding sodium acetate (Dieckmann, *Annalen* (1901), **317**, 63).

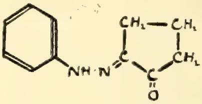
It has now been found that addition of a solution of benzene diazonium chloride to the solution obtained by treatment of ethyl cyclohexanone-2-carboxylate with one equivalent of aqueous alcoholic alkali at 0° for 24 hours, followed by addition of solid sodium acetate, leads to a rapid evolution of carbon dioxide and the separation of the expected cyclohexan-1:2-dione monophenylhydrazone (II) in almost quantitative yield. This is readily cyclised to 1-keto-1:2:3:4-tetrahydrocarbazole (1) by boiling with a mixture of glacial acetic acid and hydrochloric acid as already shown by Coffey (*loc. cit.*). It is worthy of comment that no trace of the phenyl hydrazone (II) was obtained by Jackson and Manske when they treated an aqueous alcoholic solution of the sodium derivative of ethyl cyclohexanone-2-carboxylate at once with benzene diazonium chloride, only the phenyl

Dd—December 7, 1932.

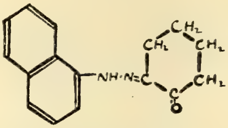
hydrazone of the half ester of α-keto-pimelic acid (IV) being obtained (*loc. cit.*, p. 5030).



IV

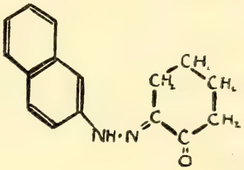


V

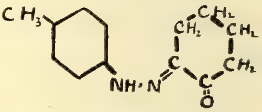


VI

In a precisely similar manner, it has been found quite easy to prepare cyclohexan-1:2-dione mono-α-naphthylhydrazone (VI), mono-β-naphthylhydrazone (VII) and

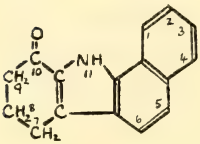


VII

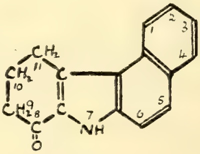


VIII

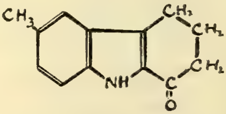
mono-p-tolylhydrazone (VIII), and to effect the cyclisation of each of these to the corresponding ketotetrahydro carbazole derivatives: 10-keto-7:8:9:10-tetrahydro-α-β-naphthacarbazole (IX), 8-keto-8:9:10:11-tetrahydro-α-β-naphthacarbazole (X), and 6-methyl-1-keto-1:2:3:4-tetrahydrocarbazole (XI), respectively.



IX



X

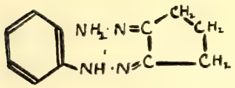


XI

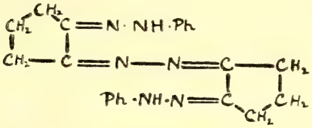
The cyclisation of the hydrazones (VI), (VII) and (VIII) could be effected by the method employed by

Coffey, but it was found much better to employ alcoholic hydrogen chloride or alcoholic sulphuric acid, cleaner products being thus obtained, which could be more readily purified.

The hydrazone derivatives (V), (VI), (VII) and (VIII) have all been further characterised by conversion into characteristic derivatives of the type described by Coffey (*loc. cit.*). Thus, treatment of (V) with alcoholic phenylhydrazine solution leads to the ready formation of the phenylosazone m.p. 146° previously prepared by Dieckmann (*Berichte* (1907), **30**, 1472) from cyclopentandione and phenylhydrazine. Treatment of (V) with hydrazine hydrate in alcoholic solution leads to the formation of the crystalline hydrazone phenylhydrazone of cyclopentan-1:2-dione (XII) obtained in apricot coloured plates m.p. 126°. Warmed with alcoholic acetic acid (XII) is rapidly transformed into cyclopentan-1:2-dione-ketazine-2:2′-diphenylhydrazone (XIII), precipitated almost at once in very sparingly soluble crimson needles which decompose without melting on heating.



XII



XIII

Similar derivatives, described in the experimental section, were obtained from the other substituted phenyl hydrazones (VI), (VII) and (VIII).

The further utilisation of the keto-tetrahydrocarbazoles so readily obtainable by the method described will be indicated in a later paper.

EXPERIMENTAL.

Cyclohexan-1:2-dione monophenylhydrazone (II).

To an ice-cold solution of ethyl cyclohexanone-2-carboxylate (36 g.; *cf.* Kötz and Michels, *Annalen*, **350**, 210; Kötz, *Annalen*, **358**, 198) in alcohol (40 cc.) was added an ice-cold solution of potassium hydroxide (12 g.) in water (60 cc.). After being kept at 0° for 24 hours ice-water (1 litre) was added to this solution, and then to the vigorously stirred resultant liquid a solution of benzene diazonium chloride (from aniline (18·6 g.), concentrated hydrochloric acid (50 cc.), water (100 cc.), and sodium nitrite (13·8 g.)) was added in one lot. Crystallised sodium acetate (30 g.) was then added. A fine yellowish-brown precipitate was at once formed and carbon dioxide was rapidly evolved. When the evolution of gas was complete the stirrer was stopped and the solid filtered off, washed with water and then recrystallised from ethyl alcohol. It was thus obtained in gleaming red-brown plates which melted at 185-186° (Coffey gives the melting point as 183-185°). The yield was practically quantitative.

Treatment of an alcoholic solution of this substance with phenylhydrazine as described by Coffey yields the characteristic phenylosazone m.p. 153-154°. Further, if boiled with a mixture of concentrated hydrochloric acid and glacial acetic acid it readily forms 1-keto-1:2:3:4-tetrahydrocarbazole (I) M.P. 169-170° (Coffey, *loc. cit.*, p. 531).

Cyclopentan-1:2-dione monophenylhydrazone (V) m.p. 203°.

This was readily obtained in an exactly similar manner (*cf.* Dieckmann, *Annalen*, **317**, 63). By boiling with an alcoholic solution of phenylhydrazine for thirty minutes it was readily converted into cyclopentan-1:2-dione

phenylosazone which crystallised on cooling in long yellow prisms melting at 146°. This substance had previously been obtained by this method, and also by treatment of cyclopentan-1:2-dione with phenyl hydrazine (Dieckmann, *Berichte* (1897), **30**, 1472).

Cyclopentan-1:2-dione hydrazone phenylhydrazone (VII).

This was obtained by adding hydrazine hydrate in excess to a suspension of cyclopentandione monophenylhydrazone in alcohol at the ordinary temperature and allowing to stand. The phenylhydrazone gradually went into solution and after some time the solution deposited pale apricot coloured plates of the hydrazone phenylhydrazone melting at 126°.

(Found C = 63·1, H = 7·2%; calculated for $C_{11}H_{14}N$, C = 65·3, H = 6·9, N = 27·7%.)

Cyclopentan-1:2-dione-1:1′-ketazine-2:2′-diphenylhydrazone (VIII).

Heating of an alcoholic solution of the above described hydrazone phenylhydrazone (VII) with acetic acid for a few minutes led to a rapid precipitation of the scarlet ketazine derivative. It is very sparingly soluble in all the usual organic solvents, but can be obtained in fine scarlet needles from much alcohol. The crystals did not melt on heating but gradually darkened to a black mass.

(Found C = 70·4, H = 6·6, N = 22·3%; calculated for $C_{22}H_{24}N_6$, C = 70·9, H = 6·5, N = 22·6%.)

Cyclohexan-1:2-dione mono-β-naphthylhydrazone.

Into an ice-cold solution of potassium cyclohexanone-2-carboxylate prepared by allowing a cold solution of ethyl cyclohexanone-2-carboxylate (26 g.) and potassium hydroxide (10 g.) in alcohol (60 cc.) and water (200 cc.)

to stand for 24 hours and then diluting with ice-water (500 cc.) was stirred a filtered diazo solution prepared from β-naphthylamine (21·5 g.), concentrated hydrochloric acid (45 cc.) and sodium nitrite (10·4 g.) in water (30 cc.). Powdered sodium acetate crystals (80 g.) were then added in one lot, the stirring being continued. A yellow precipitate was immediately thrown out and rapid liberation of carbon dioxide caused the mass to froth up. The colour of the precipitate rapidly changed through orange to dull-red in appearance, and after stirring for 30 minutes it was filtered off at the pump, washed well with cold water and recrystallised first from alcohol and then from hot ethyl acetate, in both of which solvents it is sparingly soluble even in the hot. It was thus obtained in fine orange brown shining platelets melting at 173°. Yield almost theoretical. It dissolves in concentrated sulphuric acid to an intensely coloured orange solution.

Found C = 76·0, H = 6·5, N = 11·4%; calculated for $C_{16}H_{16}ON_2$, C = 76·2, H = 6·3, N = 11·1%.)

Cyclohexan-1:2-dione-1:1′-ketazine-2:2′-di-β-naphthylhydrazone.

On warming a suspension of the above described cyclohexan-1:2-dione mono-β-naphthylhydrazone (3 g.) in alcohol with an excess of hydrazine hydrate the solid went into solution rapidly and a pale orange coloured solution resulted. Addition of glacial acetic acid (0·5 cc.) caused the colour to change to red brown, and after two or three minutes fine dull-red needles commenced to separate. These were collected, thoroughly washed with alcohol and dried. The substance was only very sparingly soluble in the usual organic solvents. It gave an orange brown solution in concentrated sulphuric

acid. It melted at 205° to a dark red liquid and decomposition commenced to occur at once.

(Found N = 17·1%; calculated for $C_{32}H_{32}N_6$, N = 16·8%.)

8-Keto-8:9:10:11-tetrahydro-α-β-naphthacarbazole (X).

A suspension of cyclohexan-1:2-dione-mono-β-naphthylhydrazone (10 g.) in alcohol (250 cc.) containing sulphuric acid (20 g.) was boiled under reflux for three hours. The hydrazone rapidly passed into solution and the colour became dark brown. The reaction liquor was finally poured into an excess of water and the solid which crystallised out was collected, well washed and recrystallised several times from alcohol. It was thus obtained in colourless prisms melting at 204-205°.

(Found C = 81·5, H = 5·7%; calculated for $C_{16}H_{13}ON$, C = 81·7, H = 5·5%.)

Cyclohexan-1:2-dione-mono-p-tolyl hydrazone.

A diazo solution prepared from p-toluidine (21·4 g.), concentrated hydrochloric acid (100 cc.) and sodium nitrite (13 g.) was filtered and rapidly stirred into a solution of potassium cyclohexanone-2-carboxylate (from ethyl cyclohexanone-2-carboxylate (35 g.), potassium hydroxide (13 g.), alcohol (80 cc.) and ice-water (800 cc.)). Addition of powdered sodium acetate crystals (100 g.) led to a rapid evolution of carbon dioxide and separation of a fine yellow precipitate which was eventually filtered off, well washed and twice recrystallised from alcohol being thus obtained in fine lemon yellow plates melting at 187°. The yield was almost theoretical.

(Found C = 72·0, H = 7·5, N = 13·4%; calculated for $C_{13}H_{16}ON_2$, C = 72·2, H = 7·4, N = 13·0%.)

This substance was but sparingly soluble in the usual organic solvents. It dissolved in concentrated sulphuric acid to an intensely red brown solution.

6-Methyl-1-keto-1:2:3:4-tetrahydrocarbazole.

Cyclohexan-1:2-dione-mono-p-tolyl hydrazone (10 g.) was boiled with a solution of concentrated sulphuric acid (20 cc.) in absolute ethyl alcohol (200 cc.) for 1 hour. The original yellow colour of the solution rapidly changed to a dirty brown and the sparingly soluble p-tolyl hydrazone soon went into solution. On cooling, the solution, which was now red-brown in colour, deposited fine needles which were collected and twice recrystallised from alcohol, being thus obtained in gleaming colourless needles melting at 195-196°. The yield was excellent.

(Found C = 78·1, H = 6·8%; calculated for $C_{13}H_{13}ON$, C = 78·4, H = 6·5%.)

Cyclohexan-1:2-dione-mono-α-naphthyl hydrazone (VI).

Addition of a filtered diazo solution from α-naphthylamine (14·3 g.), concentrated hydrochloric acid (50 cc.) and sodium nitrite (7 g.) to a cold dilute aqueous alcoholic solution of potassium cyclohexanone-2-carboxylate, prepared by hydrolysis of ethyl cyclohexanone-2-carboxylate (18 g.) with cold dilute aqueous alcoholic potassium hydroxide as above, followed by addition of crystallised sodium acetate (60 g.) led to evolution of carbon dioxide and separation of a dirty yellow precipitate of the expected hydrazone. It was collected, washed thoroughly with water and recrystallised from hot alcohol and thus obtained in dark orange-brown prisms melting at 133°.

(Found C = 75·4, H = 6·6, N = 11·3%; calculated for $C_{16}H_{16}ON_2$, C = 76·2, H = 6·3, N = 11·1%.)

The substance was readily soluble in alcohol to a deep yellowish brown solution. It dissolved readily in concentrated sulphuric acid to a very dark brownish red solution.

10-Keto-7:8:9:10-tetrahydro-α-β-naphthacarbazole (IX).

A solution of cyclohexan-1:2-dione (10 g.) in alcohol (250 cc.) containing sulphuric acid (20 g.) was boiled under reflux for three hours. The solution was then poured into an excess of cold water and the precipitated solid collected, well washed and finally recrystallised several times from alcohol, being thus obtained in minute colourless prisms melting at 238-240°. The yield was excellent.

(Found C = 81·4, H = 5·9%; calculated for $C_{16}H_{13}ON$, C = 81·7, H = 5·5%.)

The author acknowledges the assistance of Mr. L. W. Curran, B.Sc., in some of the earlier experiments of this series.

Department of Organic Chemistry,
The University of Sydney.

ABSTRACT OF PROCEEDINGS

OF THE

Royal Society of New South Wales.

MAY 4TH, 1932.

The Annual Meeting, being the five hundred and eighth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 8 p.m.

Mr. Edwin Cheel, President, in the Chair.

Thirty-seven members and three visitors were present.

The President announced the deaths of James R. M. Robertson, elected in 1924, and John Leo Watkins, elected in 1876.

The certificates of five candidates for admission as ordinary members were read: one for the second and four for the first time.

The following gentleman was duly elected an ordinary member of the Society: Francis Goulder.

The Annual Financial Statement for the year ending 31st March, 1932, was submitted to members, and on the motion of Professor Chapman, seconded by Mr. Penfold, was unanimously adopted.

ROYAL SOCIETY OF NEW SOUTH WALES.

Statement of Receipts and Payments for the Year ended 31st March, 1932.

GENERAL ACCOUNT.

RECEIPTS.

Dr.

	£	s.	d.	£	s.	d.
To Balance—31st March, 1931				915	0	7
„ Revenue—						
Subscriptions	421	14	0			
Rents	34	6	7			
Sundry Receipts	22	13	8			
Government Subsidy	300	0	0			
Interest—						
Government Bonds and Stock and Loan	610	11	0			
				1,389	5	3
„ Royal Society's Fund—Interest Added				251	12	0
„ Life Membership Fees				21	0	0
„ Bonds				2,565	5	2
				£5,142	3	0

PAYMENTS.

Cr.

	£	s.	d.	£	s.	d.
By Administrative Expenses—						
Salaries and Wages—						
Office Salary and Accountancy Fees	291	15	0			
Assistant Librarian	48	0	0			
				339	15	0
Printing, Stationery, Advertising and Stamps—						
Stamps and Telegrams	55	5	6			
Office Sundries and Stationery	3	19	5			
Advertising	18	1	0			
Printing	69	3	11			
				146	9	10
Rents, Rates, Taxes and Services—						
Rent	188	15	7			
Electric Light and Gas	12	16	6			
Insurance	24	2	6			
Telephone	18	1	8			
				243	16	3
Printing and Publishing Society's Volume—						
Printing, etc	322	6	9			
Bookbinding	47	14	0			
				370	0	9

	£ s. d.	£ s. d.
Library—		
Bookbinding	100 0 0	
Books and Periodicals	8 4 0	
		108 4 0
Sundry Expenses—		
Removal and Re-establishment Expenses	142 13 1	
Repairs	36 15 8	
Bank Charges	0 7 6	
Sundries	75 0 11	
		254 17 2
„ Interest—		
Royal Society's Fund	251 12 0	
Loans	171 19 0	
		423 11 0
„ Furniture		264 5 3
„ Science House		753 6 8
„ Loan on Mortgage—Institution of Engineers ..		333 6 8
„ Liversidge Bequest		37 10 0
„ Clarke Memorial Fund		0 11 6
„ Building Investment Loan Fund		1,783 1 9
„ Balance—31st March, 1932—		
Union Bank of Australia, Ltd. ..	£79 11 11	
Cash on Hand	3 15 3	
		83 7 2
		£5,142 3 0

Compiled from the Books and Accounts of the Royal Society of New South Wales, and certified to be in accordance therewith.

(Sgd.) HENRY G. CHAPMAN, M.D.,
Honorary Treasurer.

(Sgd.) W. PERCIVAL MINELL, F.C.A. (Aust.),
Auditor.

Sydney, 26th April, 1932.

BALANCE SHEET AS AT 31st MARCH, 1932.

LIABILITIES.

	£ s. d.	£ s. d.
Investment Fund—		
Clarke Memorial Fund	1,428 8 6	
Walter Burfitt Prize Fund ..	617 10 9	
Investment Fund	3,928 19 3	
Liversidge Bequest	550 7 2	
		6,525 5 8
On Loan		536 18 3
Sundry Liabilities		166 6 5
Accumulated Funds		28,907 13 3
		£36,136 3 7

ASSETS.

	£ s. d.	£ s. d.
Cash—		
Union Bank of Australia, Ltd. ..	79 11 11	
Cash on Hand	3 15 3	
		83 7 2
Government Bonds and Stock (Nominal Value £4770)		4,508 2 3
Science House Management Committee—		
Payments to Date		14,023 6 8
Sundry Debtors—		
Institution of Engineers	£5,283 6 8	
For Rents and Sundries	14 3 11	
For Subscriptions in Arrears ..	677 0 0	
		5,974 10 7
Library—		
Balance—31st March, 1931 ..	9,382 5 2	
Add Expenditure During Year	108 4 0	
		9,490 9 2
Office Furniture		1,716 7 9
Pictures		180 0 0
Microscopes		120 0 0
Lantern		40 0 0
		£36,136 3 7

Compiled from the Books and Accounts of the Royal Society of New South Wales, and certified to be in accordance therewith.

(Sgd.) HENRY G. CHAPMAN, M.D.,
Honorary Treasurer.

(Sgd.) W. PERCIVAL MINELL, F.C.A. (Aust.),
Auditor.

Queensland National Bank Chambers,
27 Hunter Street,
Sydney, 26th April, 1932.

INVESTMENT FUND.

Statement of Receipts and Payments for the Year ended 31st March, 1932.

RECEIPTS.

Dr.

	£ s. d.	£ s. d.
To Balance—31st March, 1931		6,290 15 2
„ Life Membership Fees		21 0 0
„ Interest—		
Clarke Memorial Fund	54 19 0	
Walter Burfitt Prize Fund ..	23 15 0	
Liversidge Bequest	22 12 0	
Investment Fund	150 6 0	
		251 12 0
		£6,563 7 2

PAYMENTS.

	£	s.	d.
By Expenditure—			
Clarke Memorial Fund	0	11	6
Liversidge Bequest	37	10	0
„ Balance—31st March, 1932	6,525	5	8
	£6,563	7	2

On the motion of Professor Chapman, seconded by Mr. Penfold, Mr. W. P. Minell was duly elected Auditor for the coming year.

The Annual Report of the Council was presented, and on the motion of Mr. C. A. Sussmilch was taken as read.

Report of the Council for the Year 1931-32.

(1st May to 27th April.)

The Council regrets to report the loss by death of five ordinary members. Twelve members have resigned. On the other hand, three ordinary members and one honorary member have been elected during the year. To-day (27th April, 1932) the roll of members stands at 293.

During the Society's year there have been eight general monthly and ten council meetings.

Four Popular Science Lectures were given, namely:

July 16: "Oysters and Oyster Culture", by T. C. Roughley.

August 20: "The Oceanographical Work of the 'S.Y. Discovery' in the Antarctic Seas", by W. W. Ingram, M.C., M.D., Ch.B.

September 17: "The Sun", by Rev. Wm. O'Leary, S.J.

October 15: "Insect Life", by W. B. Gurney, B.Sc.

Meetings were held throughout the Session by the Sections of Geology and Physical Science.

The Section of Industry during the year again devoted its attention to visiting industrial establishments.

Eighteen papers were read at the general monthly meetings.

Lecturettes were given at the general monthly meetings in June, July, August, September, November and December, by Messrs. H. G. Chapman, C. E. Fawsitt, A. R. Penfold, W. L. Waterhouse, C. A. Sussmilch and J. C. Earl respectively.

Science House.—On Wednesday evening, 6th May, 1931, the Council invited a number of visitors to the first meeting of the Society held in Science House, when the retiring President, Professor O. U. Vonwiller, B.Sc., F.Inst.P., delivered his Presidential Address entitled: "A Generation of Electron Theory."

On the afternoon of Thursday, 7th May, 1931, a representative gathering assembled at Science House, when His Excellency the Governor Sir Philip Game, G.B.E., K.C.B., D.S.O., performed the Official Opening of Science House. During the week Science House was thrown open to the public, and a large number of exhibits were displayed not only by the three owning bodies, but also by the various other scientific societies housed in Science House. This was the first exhibition of its kind ever held in Sydney and was very largely attended. During the evening sessions, popular science lectures were delivered in the large hall by the following:

Thursday, 7th May, 1931, at 8 p.m.: "The Balance of Life in the Sea", by Professor W. J. Dakin, D.Sc.

Thursday, 7th May, 1931, at 9 p.m.: "The Polar Explorations", by Instructor-Commander Moyes, B.Sc., R.A.N.

Friday, 8th May, 1931, at 8 p.m.: "What of the City", by B. J. Waterhouse, F.R.I.B.A.

Friday, 8th May, 1931, at 9 p.m.: "Prospecting by Magnetic Methods", by Major E. H. Booth, M.C., B.Sc.

Centenary Meeting of the B.A.A. Science.—Professor A. R. Radcliffe-Brown was appointed the Society's delegate at the centenary meeting of the British Association for the Advancement of Science at its meeting held in London on September 23 to 30, 1931.

First Liversidge Research Lecture.—Under the terms of the Liversidge Bequest, the first Liversidge research lecture was delivered before the Royal Society at Science House, Sydney, on Thursday, 24th September, 1931, by Mr. Harry Hey, of the Electrolytic Zinc Company of Australasia, Limited, Melbourne, entitled: "The Production of Zinc by Electrolysis of Zinc Sulphate Solutions".

Clerk Maxwell Centenary.—Professor Kerr Grant, of the University of Adelaide, and Dr. W. H. Love, of the University of Sydney, were appointed to represent the Royal Societies of Australia at the celebrations of the Clerk Maxwell Centenary held at the University of Cambridge on October 1 to 2, 1931.

Michael Faraday Centenary.—An invitation was received from the Royal Institution of Great Britain, asking the Royal Society to appoint a delegate to the Centenary of Michael Faraday's discovery of electromagnetic induction, to be held in London in September, 1931.

The Council appointed Dr. W. H. Love to represent the Society.

The Centenary was also celebrated in the Great Hall of the University of Sydney on Tuesday, September 22nd, 1931, by the Institution of Engineers, Australia, the Institution of Electrical Engineers, the Institution of Civil Engineers, the Royal Society of New South Wales and the Australian Chemical Institute. At this function addresses were given by Professors O. U. Vonwiller and J. P. Madsen.

The Proceedings of the Royal Society of New South Wales.—During the year it was decided to issue the Society's Journal in two half-yearly parts instead of one yearly part as previously, in order that papers read in the early part of the year might get quicker publicity.

At its meeting on Wednesday, 30th March, 1932, the Council awarded the *Clarke Memorial Medal* to Frederick Chapman, A.L.S., F.G.S., of the National Museum, Melbourne.

The *Annual Dinner* took place at the University Club, Phillip Street, Sydney, on Thursday, 21st April, 1932, at 6.45 p.m., when we were honoured by the presence of His Excellency the Governor Sir Philip Game, Mr. Justice Halse Rogers, Mr. R. J. Hawkes (President of the Chamber of Manufactures of New South Wales), Dr. C. Anderson (President of the Linnean Society of New South Wales), and Mr. A. P. Mackerras (representing the President of the Institution of Engineers, Australia).

The donations to the library have been as follows: 78 volumes, 2,762 parts, 47 reports, 2 maps, 8 calendars and 1 catalogue.

The President announced that the following popular science lectures would be delivered this session:

July 21: "Volcanoes", by Professor L. A. Cotton, M.A., D.Sc.

September 15: "Geophysical Prospecting", by Major E. H. Booth, M.C., B.Sc., F.Inst.P.

October 20: "The Physiological Basis of Sex Characteristics", by Assistant Professor H. Priestley, M.D., Ch.M.

November 17: "Modernism in Architecture", by James Nangle, O.B.E., F.R.A.S.

Alteration to Rule IX.—In accordance with Rule L, the following alteration to Rule IX, which had been carried at the general monthly meeting held on August 5th, 1931, was, on the motion of Mr. C. A. Sussmilch, seconded by Mr. A. R. Penfold, duly confirmed at the meeting:

> "That Rule IX be altered to read as follows: The Annual Subscription shall be Two Guineas, payable in advance, but members who are under twenty-eight years of age, and those elected prior to December, 1879, shall be required to pay only One Guinea yearly'."

Alteration to Rules to Provide for the Admission of Firms and Companies as Members.—The Hon. Secretary reported that the Council had considered the amendment suggested at the last general monthly meeting in December. These were referred back to the subcommittee who had drafted the original proposed alteration of the rules and that the Council, when considering the report of the subcommittee, had decided not to go any further with the matter.

The following donations were received: 6 volumes, 64 parts, and 5 reports.

The President, Mr. Edwin Cheel, then delivered his Address.

There being no other nominations, the President declared the following gentlemen to be Officers and Council for the coming year:

President:

Assist.-Prof. W. R. BROWNE, D.Sc.

Vice-Presidents:

Prof. J. DOUGLAS STEWART, B.V.Sc., M.R.C.V.S.	Prof. O. U. VONWILLER, B.Sc., F.Inst.P.
Prof. L. A. COTTON, M.A., D.Sc.	EDWIN CHEEL, F.L.S.

Hon. Treasurer:

Prof. H. G. CHAPMAN, M.D.

Hon. Secretaries:

C. A. SUSSMILCH, F.G.S., F.S.T.C.	R. J. NOBLE, M.Sc., Ph.D., B.Sc.Agr.

Members of Council:

E. C. ANDREWS, B.A., F.G.S.	Prof. C. E. FAWSITT, D.Sc., Ph.D.
E. H. BOOTH, M.C., B.Sc., F.Inst.P.	A. R. PENFOLD, F.A.C.I., F.C.S.
R. W. CHALLINOR, F.I.C., F.C.S.	Assoc.-Prof. H. PRIESTLEY, M.D., Ch.M.
Sir EDGEWORTH DAVID, K.B.E., C.M.G., D.S.O., F.R.S., B.A., D.Sc.	Prof. R. D. WATT, M.A., B.Sc.
Prof. J. C. EARL, D.Sc., Ph.D.	M. B. WELCH, B.Sc., A.I.C.

Mr. Cheel, the outgoing President, then installed Assist. Professor W. R. Browne as the President for the coming year, and the latter briefly returned thanks.

On the motion of Professor Vonwiller, a hearty vote of thanks was accorded to the retiring President for his valuable address.

Mr. Cheel briefly acknowledged the compliment.

JUNE 1st, 1932.

The five hundred and ninth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 8 p.m.

Professor W. R. Browne, President, in the Chair.

Twenty-five members and one visitor were present.

The certificates of the following candidates for admission as ordinary members were read for the first time: Kenn. P. Forman, Refrigeration Engineer, Electricity Meter Manufacturing Co., Waterloo, and Ivor Vickery Newman, M.Sc., Ph.D., F.R.M.S., F.L.S., Kingsland Road, Strathfield.

The President nominated Mr. Cheel to preside at the ballot box, and members elected Messrs. A. D. Olle and F. Morrison to act as scrutineers.

According to Rule V, "no ballot for the election of members of Council, or of new members shall be valid unless twenty members at least shall record their votes". Only thirteen members voted, thus the election was invalid.

The following donations were received: 9 volumes, 266 parts and 6 reports.

THE FOLLOWING PAPERS WERE READ:

1. "The Mitotic Activity of Normal and Malignant Tissues and its Modification by X-Rays", by W. H. Love, B.Sc., Ph.D. (Illustrated by lantern slides.)
2. "The Chemical Changes Involved in the Formation of Aminoazo Compounds", Part I, by Professor J. C. Earl, D.Sc., Ph.D., and Norman Frederick Hall, B.Sc.
3. "A Note on the Action of Titanium Tetrachloride on Tetracetyl-β-d-Glucoside-Glycollic Ester", by Miss Thelma M. Reynolds, M.Sc. (Communicated by Professor J. C. Earl.)
4. "Researches on Indoles", Part II, by Francis Lions, B.Sc., Ph.D., and Miss Mary J. Spruson.

EXHIBIT:

Dr. R. J. Noble exhibited a case showing mushrooms developed under artificial conditions at the Biological Branch, Department of Agriculture, Sydney.

Pure culture spawn had been prepared from tissue cultures and from spores; the test case was spawned on the 20th April, cased with soil on the 3rd May, and the first crop of mushrooms had appeared on the 1st June.

JULY 6th, 1932.

The five hundred and tenth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, at 8 p.m.

Professor W. R. Browne, President, in the Chair.

Thirty-one members and three visitors were present.

Alteration of Time of Monthly Meetings.—The President announced that the Council at its last meeting had decided that in future the monthly meetings would be started at 7.45 p.m., so that the formal business might be completed by 8 p.m., and thus give more time for papers, discussions and lecturettes.

The President announced that the following members had been honoured: Dr. Frederick William Wheatley, C.B.E., Commander of the Order of the British Empire; Dr. Allan R. Callaghan, appointed to the position of Principal of the Roseworthy Agricultural College, Adelaide; and Mr. R. L. Aston, the degree of Doctor of Philosophy by the Cambridge University.

The certificates of candidates for admission as ordinary members were read: six for the second two for the first time.

The following gentlemen were duly elected ordinary members of the Society: Kenn. P. Forman, Arthur

Thomas Keeble, Ernest Norman McKie, Erik Munch-Petersen, Ivor Vickery Newman and Henry Elmar Richardson.

The following donations were received: 9 volumes, 200 parts and 12 reports.

THE FOLLOWING PAPERS WERE READ:

1. "The Occurrence of a Number of Varieties of *Eucalyptus radiata* (*E. numerosa*) as Determined by Chemical Analyses of the Essential Oils", Part I, by A. R. Penfold, F.C.S., and F. R. Morrison, F.C.S.
2. "Studies of the Intrusive Igneous Rocks of the Muswellbrook-Singleton District", Part II. The Savoy Sill. By H. G. Raggatt, M.Sc., and H. F. Whitworth, B.Sc.
3. "The Crystal Structure of Indium", by Francis P. Dwyer, B.Sc., and David P. Mellor, M.Sc.

Symposium: "The Constitution of the Earth", opened by Major E. H. Booth and Professor L. Cotton.

Professor Vonwiller and the President also contributed to the symposium.

AUGUST 3rd, 1932.

The five hundred and eleventh General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, 7.45 p.m.

Professor W. R. Browne, President, in the Chair.

Twenty-eight members and five visitors were present.

The President announced the death of Sir Richard Threlfall, who had been an honorary member of the Society since 1921.

The certificates of four candidates for admission as ordinary members were read: two for the second and two for the first time.

The following gentlemen were duly elected ordinary members of the Society: John Patrick O'Neill and Victor Martin Trikojus.

It was announced that the Council had awarded the "Walter Burfitt Prize" for 1932 to Dr. Charles Halliby Kellaway, Director of the Walter and Eliza Hall Institute of Research in Pathology and Medicine, for research work published during the three years 1929 to 1931, and that the presentation would take place at Science House on Tuesday, 16th August, 1932, at 4 p.m.

The following donations were received: 3 volumes, 104 parts and 3 reports.

THE FOLLOWING PAPERS WERE READ:

1. "The Chemistry of Western Australian Sandalwood Oil", Part II, by A. R. Penfold, F.A.C.I., F.C.S.
2. "Ripple-Marks in the Narrabeen Series along the Coast of New South Wales", by Alma G. Culey, B.Sc. (Communicated by Professor L. A. Cotton.)
3. "Derivatives of 2-Phenyl Quinoline", Part I. Preparation of Some "Atophans" from Veratric Aldehyde, by Muriel Gertrude Holdsworth, M.Sc., and Francis Lions, B.Sc., Ph.D.

LECTURETTE:

"Some Recent Research in Anaerobic Infections in Domestic Animals", by H. R. Carne, B.V.Sc.

SEPTEMBER 7th, 1932.

The five hundred and twelfth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Professor W. R. Browne, President, in the Chair.

Twenty-five members and two visitors were present.

The President announced the death of Mr. Ernest Le Gay Brereton, who was elected a member in 1923.

The following gentlemen were duly elected ordinary members of the Society: Herbert Eril Boon and Ralph Charles Bradley Lane.

The following donations were received: 299 parts, 11 volumes, and 9 reports.

THE FOLLOWING PAPERS WERE READ:

1. "A Note on the Constitution of Tasmanol", by V. M. Trikojus, B.Sc., D.Phil., and D. E. White, M.Sc.
2. "The Chemistry of the Constituents of the Wood-Oil of the 'Callitris' Pines", by V. M. Trikojus, B.Sc., D.Phil., and D. E. White, M.Sc.
3. "The Synthesis of Bases Allied to Coniine", Part I. The Preparation and Pyrolysis of the Allyl Ethers of N. Heterocyclic Enols, by Burnett Mander-Jones, M.Sc., and V. M. Trikojus, B.Sc., D.Phil.
4. "The Use of Potassium Dichromate and Sodium Nitrite in Aromatic Nitrosations", by F. P. J. Dwyer, B.Sc., D. P. Mellor, M.Sc., and V. M. Trikojus, B.Sc., D.Phil.
5. "The Essential Oils of Three Species of Geijera and the Occurrence of a New Hydrocarbon", Part II, by A. R. Penfold, F.A.C.I., and Professor J. L. Simonsen, D.Sc., F.R.S.

LECTURETTE:

"White Ants and Their Ravages", by M. B. Welch, B.Sc. (Illustrated by lantern slides.)

OCTOBER 5th, 1932.

The five hundred and thirteenth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, at 8 p.m.

Professor W. R. Browne, President, in the Chair.

Forty members were present.

The following donations were received: 144 parts, 7 volumes and 3 reports.

THE FOLLOWING PAPER WAS READ:

"Note on the Internal Structures of *Barrandella* and *Sieberella*", by F. W. Booker, M.Sc.

SYMPOSIUM:

"Phosphorus in Nature."

The symposium was carried out by L. L. Waterhouse (Geology), Professor R. D. Watt (Agriculture), Professor J. Douglas Stewart (Veterinary Science), and Associate Professor Priestley (Physiology).

NOVEMBER 2nd, 1932.

The five hundred and fourteenth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Professor W. R. Browne, President, in the chair.

Thirty-five members and three visitors were present.

The following donations were received: 69 parts, 8 volumes, 3 reports and 1 calendar.

THE FOLLOWING PAPERS WERE READ:

1. "Notes on the Mineralogy of the Narrabeen Series of New South Wales", by Miss Alma G. Culey, B.Sc. (Communicated by Professor L. A. Cotton.)

2. "A Note on the Occurrence of β-Cristobalite in Australian Opals", by F. P. Dwyer, B.Sc., and D. P. Mellor, M.Sc.
3. "An Average Moisture Equilibrium for Wood", by M. B. Welch, B.Sc.
4. "The Quantitative Theory of Interaction Between Different Species of Animals", by Associate Professor V. A. Bailey, M.A., D.Phil.

ADDRESS:

By Mr. A. B. Hector: "Some Thoughts on the Improvement of our Education System."

DECEMBER 7th, 1932.

The five hundred and fifteenth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, at 8 p.m.

Thirty-three members and one visitor were present.

The certificate of one candidate for admission as an ordinary member was read for the first time.

The following donations were received: 499 parts, 17 volumes, 6 reports and 1 calendar.

Mr. A. R. Penfold gave notice that at the next meeting he would move:

> "In lieu of present Rule X: 'The first annual subscription shall accompany the prescribed form of certificate for admission. The election will not be proceeded with unless this condition is fulfilled.' "

THE FOLLOWING PAPERS WERE READ:

1. "Relation of the Tertiary Alkaline Rocks of Eastern Australia to Late Tertiary Tectonic Lines", by C. A. Sussmilch, F.G.S.
2. "A Possible Correlation of Certain Pre-Cambrian Granites of Australia and Some Deductions Therefrom", by Professor W. R. Browne, D.Sc.
3. "The Essential Oil from the Wood of *Eremophila Mitchelli* (Bentham)", by A. E. Bradfield, Ph.D., A. R. Penfold, F.A.C.I., and Professor J. L. Simonsen, D.Sc., F.R.S.
4. "An Examination of the Validity of Conclusions Drawn from Experiments in which the Allantoic Membrane of the Chick is Exposed to X Radiation", by Warnford Moppett, M.D., Ch.M.
5. "The Chemical Changes Involved in the Formation of Aminoazo Compounds", Part II, by Professor J. C. Earl, D.Sc., Ph.D., and N. F. Hall, B.Sc.
6. Derivatives of 2-Phenyl-Quinoline", Part II. Some "Atophans", with Substituent Basic Groups, by Muriel G. Holdsworth, M.Sc., and Francis Lions, B.Sc., Ph.D.
7. "Derivatives of 2-Phenyl-Quinoline", Part III. Some Derivatives of Polyhydroxy "Atophans", by Muriel G. Holdsworth, M.Sc., and Francis Lions, B.Sc., Ph.D.
8. "An Extension of Knorr's Pyrrole Synthesis", by Gregory Bondietti, M.Sc., and Francis Lions, B.Sc., Ph.D.
9. A Note on Diffration Gratings Used with Grazing Incidence", by Professor O. U. Vonwiller, B.Sc., F.Inst.P.

10. "Longitudinal Variation of Timber during Seasoning", by M. B. Welch, B.Sc.
11. "Experiments on the Daily Shrinkage and Swelling of Wood", by M. B. Welch, B.Sc.
12. "Application of Optical Spectroscopy to Analysis of Tumour Tissue", by Winifred R. Mankin, B.Sc. (Communicated by Professor O. U. Vonwiller.)
13. "Researches on Indoles", Part III, by Francis Lions, B.Sc., Ph.D.

ABSTRACT OF THE PROCEEDINGS

OF THE

GEOLOGICAL SECTION.

ANNUAL MEETING, APRIL 29th, 1932.

Mr. C. A. Sussmilch was in the chair; eleven members and nine visitors were present.

Mr. W. S. Dun was elected Chairman and Mr. H. G. Raggatt, Secretary for the year.

Dr. G. D. Osborne addressed the Section on "Current Geological and Mineralogical Research in Europe".

After briefly stating the scope of his travels in the British Isles and Western Europe, the speaker gave an outline of the general progress of current research, as he observed it, in the various divisions of geology, mineralogy and petrology.

MAY 20th, 1932.

Mr. W. S. Dun was in the Chair; ten members and three visitors were present.

EXHIBITS:

1. By Dr. G. D. Osborne. Two suites of rocks illustrating the Carboniferous and Permian (?) igneous activity of the Midland Valley of Scotland.
2. By Mr. H. G. Raggatt. Glendonites of an unusual type from Flagstaff Hill, Wollongong.

Three short addresses, illustrated by specimens, maps and diagrams, were given:

1. By Mr. L. J. Jones: "On the Distribution of Commercial Coal in the Borehole Seam, Newcastle District."

2. Mr. F. W. Booker exhibited and described the principal features of interest attached to certain fossils from the Upper Marine series of the Hunter Valley (N.S.W.) and from the Bowen River District (Q.).

3. Mr. H. G. Raggatt briefly described the geology of the Wingen District.

The principal points referred to were: (i) A section at Owen's Gap, showing rocks which might be referred to the Jurassic; (ii) Tertiary intrusives near Wingen, including the Bosley's Gully volcanic neck and the Murulla dolerite-basalt composite sill; (iii) the position of the Wingen fault which is placed west of the Burning Mountain instead of east of it, as formerly; (iv) conformability of Kuttung and Kamilaroi.

JUNE 17th, 1932.

Mr. W. S. Dun was in the Chair; ten members and ten visitors were present.

EXHIBITS:

1. By Mr. H. F. Whitworth: (i) Coarse and massive sillimanite rock from Thackaringa, 20 miles N.W. from Broken Hill; (ii) staurolite schist from the same locality.
2. By Dr. G. D. Osborne. From Seaham, varves with annelid tracks, raindrop impressions and ripple marks; specimen showing intraformational pavement in varve rock and specimens showing parallel furrows produced by icebergs moving over plastic varves.

DISCUSSION:

"On the Distribution and Origin of 'Grey Billy' and Related Siliceous Rocks."

Mr. Kenny introduced the subject by a general statement in which he grouped the materials under two major divisions:

(*a*) Those associated with igneous extrusions. Examples: the masses of siliceous material beneath basalt sheets, as in New England, Dubbo-Dunedoo, Coonabarabran, Gunning, and other places.

(*b*) Chemically formed masses exemplified in western New South Wales, at Tallong, and at Ulladulla.

Particular attention was given to the occurrences of "Grey Billy" in western New South Wales. Mr. Kenny mentioned the pre-eminent relationship of siliceous cappings to developments of clayey sandstones and gritty clays of the Eyrian Series (Tertiary); outlined the mode of occurrence, structure and lithology of the "Grey Billy", and concluded by remarking upon the time relationship of the material to the Eyrian Series on the one hand and to the post-Tertiary beds on the other. He produced evidence to show that the "Grey Billy" pre-dated the Pleistocene sediments, being found at depth in bores and wells, and post-dated the Eyrian Series of Lower Tertiary Age. A Tertiary, possibly pre-Miocene age, was assigned to the "Grey Billy".

Continuing the discussion, Professor W. R. Browne dealt mainly with the "Grey Billy" associated with lava-flows, in which the cementing silica, mostly as quartz, was due probably to volcanic hot-spring deposition mostly among loose sands. The opal found with this type of "Grey Billy", as at Tallong, might have been deposited from alkali carbonate solutions. The similarity between this "Grey Billy" and that from White Cliffs *et cetera*, was stressed.

Mr. Whitworth then described the microscopical structure of the typical western district type of "Grey Billy", stating that most of them consist mainly of angular quartz grains with an almost opaque cementing material which was known to contain opaline silica and free alumina. It was suggested that the groundmass might represent a clay which had split up into free silica and alumina during some process of weathering during a period of peneplanation which prevented the run off of the dissolved silica. Under such conditions the silica would be carried downwards and be deposited around sand grains, or be

precipitated by clays, forming the secondary quartzites at some little depth below the surface in a manner analogous to the formation of ironstone nodules in the Tertiary soils around Sydney.

Mr. L. L. Waterhouse exhibited and discussed a suite of specimens from near the head of Badgery's Track, Tallong, including (in descending order) fresh massive olivine basalt, decomposed very vesicular basalt, "Grey Billy" with quartz cement containing plant remains, "Grey Billy" with chalcedonic cement, "Grey Billy" with opaline cement. The latter rests with a very sharply defined lower boundary upon unconsolidated Tertiary sands, and these in turn upon massive Kamilaroi gritty sandstones.

JULY 15th, 1932.

Mr. W. S. Dun was in the Chair. Ten members and a number of visitors were present.

EXHIBITS:

1. By Dr. Ida Brown. Limestone with *Pentamerus knightii,* from Baw Baw, about 4 miles west of Goulburn.
2. By Mr. W. S. Dun. Specimens of *Spirifera striata* from Hilldale and England; *Spirifera tasmaniensis* and *S.* (*Trigonotreta*) *stokesi* from Anvil Creek, N.S.W.
3. Assistant Professor W. R. Browne. Dolerite from Prospect with analcite containing spherules of radiating chlorite.
4. By Mr. L. L. Waterhouse. From the Limekilns, Marulan: (*a*) intraformational breccia, silicified and silicated, from the Silurian between the eastern and western limestone belts; (*b*) fault breccia from east of the eastern limestone; (*c*) fossiliferous Silurian limestone from the eastern belt, the Lookout, Bungonia.

5. By Dr. G. D. Osborne. A series of specimens from Barnavarve, Carlingford (Ireland), illustrating the hybridism between acid and basic igneous rocks of the Tertiary ring-dyke of that area.
6. By Mr. T. Hodge Smith, on behalf of the Australian Museum. (*a*) Epsomite from Nelly's Glen, Katoomba. (*b*) Barytes in pegmatite, Thackaringa. (*c*) Jasper from Marble Bar (W.A.). (d) Cassiterite from Stoney's Creek (Tas.). (*e*) Barytes from the Barrier Ranges.
7. By Mr. H. G. Raggatt. (*a*) Bone cores of volcanic breccia from Lower Marine, Muswellbrook. (*b*) *Chœnomya audax* from the centre of a concretion, Flagstaff Hill, Wollongong.
8. By Mr. H. F. Whitworth. (*a*) A collection of synthetic gems and the boules from which they are cut. These are mainly varieties of coloured corundum and aluminates. (*b*) Plumose rhodocrosite. (*c*) A natural beach sand concentrate from Rabaul composed largely of augite, hornblende and olivine.
9. By Mr. L. W. Morris. Synthetic crystals of bismuth formed by crystallization in a cavity allowing of uninterrupted growth.

SEPTEMBER 16th, 1932.

Mr. W. S. Dun was in the Chair; eleven members and nine visitors were present.

EXHIBITS:

1. By H. F. Whitworth. A specimen of Bulli coal polished and etched by Seyles's method, showing cell structure in wood.
2. By Assistant Professor W. R. Browne. Specimens from near Michelago, showing a sudden change

within six feet from dipping Silurian limestone to rhyolite tuffs along the strike.

3. By Dr. C. Anderson. A slug of tinstone from alluvials near Zeehan, Tasmania.

Mr. E. C. Andrews then addressed the Section on "The Physiography and Tectonics of Australia in Relation to the Rest of the World".

A general survey was given of the geomorphology of the various continental masses, particular attention being paid to the physiographic features associated with the highland belts found around the margins of the Pacific, and also to the mountain belts of Europe and India (particularly the Himalayan region). The relation of the mountain arcs to the associated lowland tracts and ocean foredeeps was described in some detail, special attention being paid to the structures of the Himalayas as illustrated by a north-south section.

A discussion of the physiographic unity of eastern Australia and the position and relationships of the Australian arc relative to the framework of the Pacific, followed.

The dependence of the structural features upon isostatic equilibrium was emphasised.

OCTOBER 21st, 1932.

Mr. W. S. Dun was in the Chair; eight members and seven visitors were present.

EXHIBITS:

1. By Mr. L. L. Waterhouse. Crystals of newberyite (hydrated phosphate of magnesia) and of struvite (hydrated phosphate of ammonia and magnesia) from Mt. Wedderin, near Skipton, Victoria. These minerals occur in loose basaltic soil and are connected with ancient guano deposits.
2. By Dr. G. D. Osborne. (*a*) Varves of Pleistocene age, Lake Ragunda, Central Sweden. (*b*) Varve clays (Pleistocene) from Achill Id., Ireland.

Professor L. A. Cotton gave an address on "Some Recent Observations on the Great Tokyo Earthquake".

Immediately following the earthquake, extensive observations dealing with its geological, seismological and geodetical aspects were made to ascertain its cause and examine its effects. Records from numerous seismological stations in Japan enabled the chief focal area to be defined with great accuracy, and this was found to lie in the submarine extension of a rift valley in the Bay of Sagami, a little to the north of the Island of Oshima.

The geological structure of the shaken area showed that it is heavily faulted, making it particularly susceptible to movement. A topographic survey revealed that there had been both vertical and horizontal movements of the land of rather less than ten feet. A survey of the floor of the Sagami Bay, however, showed astounding changes in level, some parts being elevated about 800 and others depressed about 1,300 feet. When the magnitude of these changes was realised, special care was taken to eliminate errors in measurement, and the results were confirmed.

NOVEMBER 18th, 1932.

Mr. W. S. Dun was in the Chair; nine members and nine visitors were present.

EXHIBITS:

1. By Mr. H. F. Whitworth. (*a*) Chiastolite flakes. (*b*) Native arsenic from Forbes. (*c*) Limestone.
2. By Mr. H. G. Raggatt. A suite of rocks representative of schists from Sebastopol, 10 miles south of Temora, probably of Ordovician age.

A discussion "On the Evolution of the Coastal Physiography of New South Wales, with Special Reference to the Development of the Present Coastline" was opened by a statement by Assistant Professor W. R. Browne. He referred principally to examples of apparent exceptions to the physiographic unity of coastal New South Wales to the universality of the Kosciusko movement. A number of sections were referred to by way of illustration.

Mr. E. C. Andrews considered that most of the apparent exceptions could be explained as variations upon a simple theme and referred specifically to some of the sections quoted by Professor Browne.

Mr. C. A. Sussmilch supported Mr. Andrews's views, and referred mainly to some Queensland examples and to the Hunter region of New South Wales.

Dr. Ida Brown referred to her work on the South Coast of New South Wales.

Dr. G. D. Osborne and Mr. H. G. Raggatt also spoke, principally with reference to the Hunter Valley.

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

PHYSICAL SCIENCE.

OFFICERS:

Chairman: Major E. H. Booth.

Hon. Secretary: Dr. W. H. Love.

Assistant Hon. Secretary: Mr. S. E. Williams.

Committee: Professors O. U. Vonwiller, V. A. Bailey, G. H. Briggs, J. P. Madsen, E. M. Wellisch, Mr. Brown.

Nine meetings were held during 1932.

15th June, 1932.—Dr. W. H. Love: "Some Quantitative Methods in Biophysics".

6th July, 1932.—Mr. J. M. Rayner, B.Sc., A.Inst.P.: "Cosmic Radiation".

20th July, 1932.—Professor O. U. Vonwiller: "The Influence of Diffraction Phenomena in Photometric Spectroscopy".

3rd August, 1932.—Mr. J. C. Jaeger, B.A., B.Sc.: "The Photo-Electric Effect in Metals".

23rd September, 1932.—(1) Mr. J. B. Rudd: "A Note on the Motion of Electrons in Gases". (2) Professor V. A. Bailey: "Some Problems in the Mathematical Theory of Mendelian Selection".

5th October, 1932.—Mr. D. P. Mellor, M.Sc., "X Rays and Crystal Structure".

19th October, 1932.—Dr. W. G. Baker: "Some Aspects of Radio Valve Design".

2nd November, 1932.—Dr. A. J. Canny: "Some Physical Aspects of Muscular Activity".

9th November, 1932.—Professor G. H. Briggs: "Some Recent Advances in the Investigation of Nuclear Structure".

ABSTRACT OF THE PROCEEDINGS

OF THE

SECTION OF INDUSTRY.

OFFICERS:

Chairman: A. D. Olle, F.C.S.
Hon. Secretary: H. V. Bettley-Cooke, F.C.S.

During the year the following works were visited by the members:

Tuesday, 10th May.—Electricity Meter Manufacturing Co., Ltd., Waterloo.

Tuesday, 14th June.—Technological Museum, Ultimo.

Tuesday, 9th August.—Taronga Park, Mosman.

Tuesday, 14th September.—Pick-Me-Up Condiment Co., Newtown.

Tuesday, 11th October.—British-Australian Lead Manufacturers Pty. Ltd., Cabarita.

Tuesday, 29th November.—R.M.S. *Strathnaver*.

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